

Metal Complexes of Indigo and of Some Related Ligands^[1]

Wolfgang Beck^{*[a]} and Karlheinz Sünkel^[a]

Dedicated to the Memory of Professor Wolfgang Lüttke (1919–2018)

Abstract. While the first coordination compounds of indigo were reported over 100 years ago, a systematic study of the coordination chemistry of this important dye and also its structural “relatives” remained silent for over half a century. Only in the last two decades of the 20th century research on this topic started again keeps on growing

ever since. It could be established, mainly by X-ray crystallography, but also by many other modern spectroscopic techniques, that deprotonated indigo, and its deprotonated oxidized and reduced forms act as mono- and bidentate chelate ligands in metal complexes

1 Early Work on Indigo and its Metal Complexes

The constitution of indigo was – after work for 16 years – solved by *Adolf von Baeyer* in Munich,^[2] and is considered as the most difficult chemical enterprise at that time.^[3] Presumably, the right formula of indigo was first formulated by *Baeyer* – rather incidentally – in his letter to *H. Caro* at BASF in 1883 (Figure 1).^[4]

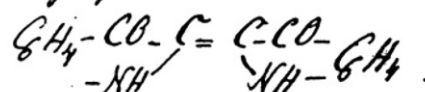
The blue color of indigo could be interpreted by *Lüttke* and *Klessinger*,^[5] also by synthesis of the “Urindigo”, the 4,4,4',4'-tetramethyl-2,2'-bipyrrolidinylidene-3,3'-dione, a compound with the stem chromophore (OC)(NH)C=C(NH)(CO).^[6] Its structure has been recently determined by X-ray diffraction^[7]

The first metal complex of indigo was reported by *Binz* in 1901:^[8] Indigo was reacted with zinc powder and *Binz* schemed this reaction as: “Indigblau + Zink = Indigweisszink”. Today we can identify the product of this reaction, which was repeated by *Kunz*^[9] and by *Kuhn* and *Machemer*,^[10,11] as zinc(II) complex with the anion of the reduced indigo (Indigoküpe) (Scheme 1)

Kunz and his co-workers studied the reactions of indigo with zinc, copper, nickel, and sodium and pentacarbonyliron. Although *Kunz* assumed in his first publication,^[9] that in these reactions hydrogen in the NH groups was substituted by metals, he later formulated the products as adducts of neutral indigo with metals or with Fe(CO)₅, respectively, because the formation of hydrogen could not be detected in these reactions.^[12,13] *Kuhn* and *Machemer*^[10,11] finally came to the right

Am 11. Apr. 1883 an H. Caro in Basel,
Sond. d. ungelösten Indigo ist vorzupfeifen,
sonst ist weiter nicht möglich.

Indigo ist:



Wie geht es denn Ihrer Arbeit?
Ich habe zu meinem größten Leid
dennoch gehört, daß Sie trübselig
aussehen ist.

Wenn Sie können telegraphieren
Sie auf bitte mit Angabe des Inhalts.
In größter Eile Ihr allzeit
treuer Mitarbeiter

Adolf Baeyer.

Figure 1. Letter of A. von Baeyer to H. Caro in 1883.

conclusion that metal complexes of indigo are Werner type *trans-N,O*-chelates (Scheme 2), which was admitted by *Kunz*.^[14]

The product of the reaction of indigo with pentacarbonyliron was considered by *Kunz*^[13] as model for hemoglobin to add oxygen reversibly. *Larkworthy*^[15] could show, that O₂ uptake by the iron(II)-indigo complex is irreversible. For the extremely oxygen sensitive iron indigo complex a magnetic moment of 5.1 B.M. was determined. A structure for the “bis-indigo iron” complex with a monoanionic indigo ligand and monoanionic reduced indigo ligand (indigo white) seems to be

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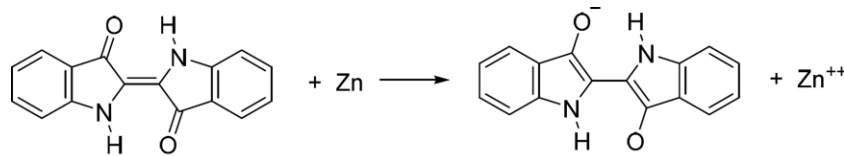
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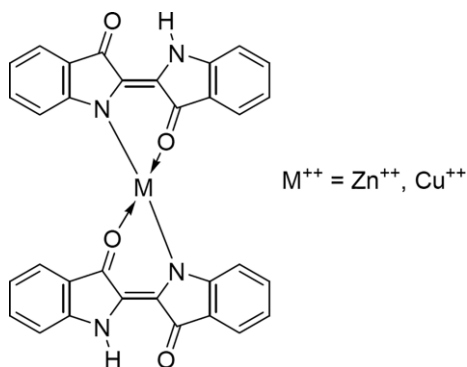
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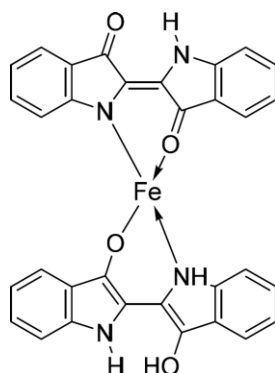


Scheme 1. The first synthesis of an indigo zinc complex.



Scheme 2. Presumable structures of the first indigo bischelates.

consistent with the experimental data, which showed four active hydrogen atoms and gave indigo blue on addition of acids (Scheme 3),^[15] which was observed also by *Hieber* and *Sonnekalb*^[16]



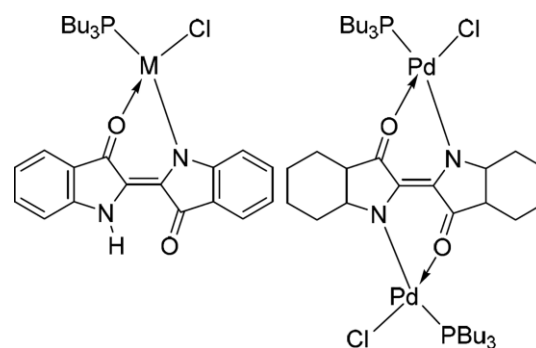
Scheme 3. Presumable structure of the reaction product from Fe(CO)₅ with indigo.

2 Modern Coordination Chemistry of Indigo and its Substituted Derivatives

2.1 Deprotonated Trans-Indigo as a N,O Chelating Ligand

For a long time – about 40 years, with one exception^[15] – no attention has been paid to complexes of indigo. After many unsuccessful attempts – due to the very low solubility of indigo in common solvents – our group in Munich succeeded to obtain crystalline indigo complexes by introduction of tri(*n*-butyl)phosphine ligands and by use of chlorido bridged complexes in the presence of Ag-acetate or NaH.^[17] In our groups chlorido bridged complexes have been proven most useful in many cases for the synthesis of novel metal complexes, e.g. of

amino acids.^[18] The structures of the *N,O*-chelate complexes [(*n*Bu₃P)(Cl)M(indigo-H⁺)] (M = Pd, Pt) and of [(*n*Bu₃P)(Cl)Pd(octahydroindigo-2H⁺)Pd(*n*-PBu₃)(Cl)] could be determined by X-ray crystallography (Scheme 4).^[17]

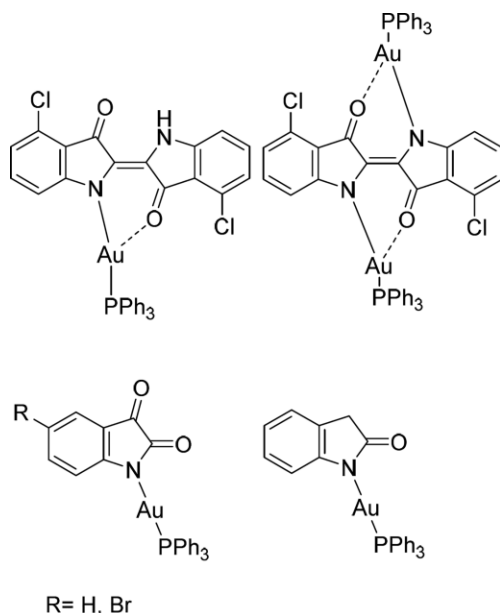


Scheme 4. Mono-deprotonated indigo as mono-chelating and bis-deprotonated octahydroindigo as bischelating ligands.

A series of similar complexes with the monoanion of disubstituted indigo derivatives IndR₂ (R = Cl, Br, OMe, *t*Bu, SO₃Na), using chlorido bridged Pd complexes [L_nPd(μ-Cl)]₂ [L_n = (PR₃)Cl, (η³-allyl), (azobenzene-H⁺), (C₆H₄CH₂NMe₂), (Cp)Fe(C₅H₃CH₂NMe₂), (Ph₂C=NCH₂CO₂Et-H⁺)], has been prepared in our group.^[19] Dimers with the dianionic indigo bridge were obtained by reaction of indigo and substituted indigo with several chlorido bridged Pd and Pt complexes.^[17,19] The structure of [(Et₃P)(Cl)Pt(indigo-2H⁺)Pt(Cl)(PEt₃)] has been determined by X-ray diffraction.^[19]

The NH protons in 4,4'-dichloroindigo could be exchanged by Schmidbaur's auring agent [(Ph₃P)Au]⁺^[21] to give [(Ph₃P)Au(4,4'-dichloroindigo-H⁺)] and [(Ph₃P)Au]₂[μ-(4,4'-dichloroindigo-2H⁺)] (Scheme 5).^[22] The structure of the gold(I) complex with the monoanion of dichloroindigo was characterized by X-ray diffraction and shows centrosymmetric pairs of molecules with parallel arrangement of the two indigo ligands in the crystal. The same arrangement has been observed for [nBu₃P)(Cl)Pd(indigo-H⁺)]^[17] Also, Ph₃P-gold complexes with the “half molecules” of indigo, isatin, 5-bromoisatin, and 2-indoline have been obtained.^[22] The structure of the isatin-gold complex was determined by X-ray diffraction.^[23] Similar gold(I) complexes have been reported with the anions of hydantoin,^[24] of PPP dyes^[25] and of various other N-heterocycles.^[26]

In our group, experiments^[27] have been carried out to use the benzene ring of indigo as π donor in metal complexes. For this purpose, indigo and some substituted indigo derivatives were treated with [Cp*⁺Ru(CH₃CN)₃]⁺ OTf⁻.^[28]



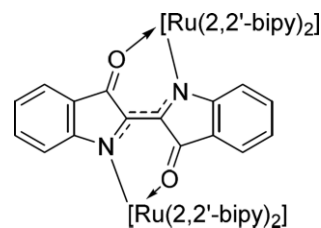
Scheme 5. Gold complexes of dichlorindigo, isatin and indoline.

About 20 years after our studies on metal complexes of indigo, this chemistry again found attention and interest by various groups (Lu, Kaim, Lahiri, Konarev, Guo, Caulton, Hicks and their co-workers), who succeeded to synthesize and determine the structure of novel indigo metal complexes with special emphasis on their redox activity.

In a hexakis(tricarbonylrhenium) complex, in which the rhenium atoms are bridged by three trispyridyl-triazines three indigo dianions act as pillars to give a triangular metalloprism. Each rhenium atom is coordinated by three CO ligands, by one pyridyl N-atom and by the dianionic *N,O*-indigo chelate ligand in this novel compound, which absorbs strongly in the near infrared region. It also reveals interesting redox chemistry, as by reduction a series of highly stable (radical) species is formed.^[29,30]

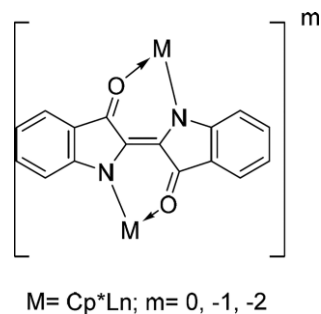
2.2 Redox Chemistry of Indigo Complexes

Following Jorgensen's remarkable arguments,^[31] Kaim^[32,33] and Lahiri^[34] have classified indigo as "noninnocent ligand", because the indigo complexes easily undergo reduction and oxidation processes. Octahedral ruthenium(II) complexes [(L-L)Ru(indigo-H⁺)]⁺ and [(L-L)Ru(indigo-2H⁺)Ru(L-L)]²⁺ with monoanionic and dianionic (bridging) indigo ligands and with 2-phenylazopyridine and bipy ligands (L-L) were synthesized and structurally characterized,^[33,35] including the first, isolable radical complex of indigo [(bipy)Ru(indigo-radical-2H⁺)Ru(bipy)]³⁺ (Scheme 6).^[34] The redox chemistry of these complexes, including several oxidation and reduction processes with radical intermediates has been extensively studied and was accompanied by theoretical calculations.



Scheme 6. The first radical complex of indigo.

By reaction of allyl-bis(pentamethylcyclopentadienyl)lanthanides with indigo and consecutive reduction with KC₈ the indigo bridged complexes [(Cp*)Ln(indigo-2H⁺)Ln(Cp*)]^m (Ln = Gd, Dy; *m* = 0, -1, -2) (Scheme 7) could be obtained and characterized by X-ray structural analysis. The indigo radical bridged gadolinium complex, which was obtained through one electron reduction of the neutral complex, exhibits strong anti-ferromagnetic coupling of the lanthanide ion with the trianionic radical indigo. The interaction between Gd³⁺ and the radical indigo ligand is the largest known for a lanthanide complex. The dysprosium complexes with *m* = 0 and 2 were shown to be single-molecule magnets in zero applied field.^[36]

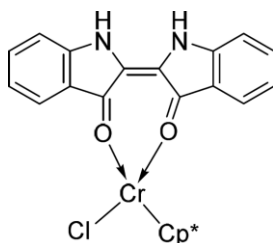


Scheme 7. Indigo as redox active ligand bridging two lanthanoid ions.

Indigocarmine (5,5'-indigodisulfonic acid-disodium salt) was reacted with hexachlorocyclodiphosph(V)azane Cl₃P(NR)₂PCl₃ to give P-bridged di-indigocarmines, from which Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Fe^{III} complexes were obtained. It was proposed that in these complexes the metal ions are *N,O*-indigo coordinated. The magnetic moments and the antimicrobial activity of the metal compounds were studied.^[37] Furthermore, metal compounds with the dianion of indigocarmine and with Cr^{III}, Cu^{II}, Ag^I, Zn^{II}, and Cd^{II} were reported.^[38]

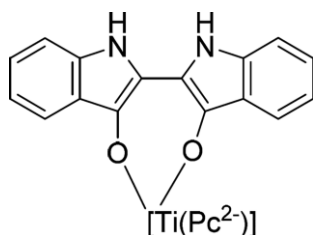
2.3 Cis-Indigo as *N,N* and *O,O* Chelating Ligand

The indigo complexes, discussed so far, exhibit the indigo ligand in *trans* configuration. Some complexes are known with the indigo ligand in *cis* configuration: By reaction of (pentamethylcyclopentadienyl)₂Cr with indigo in the presence of a chloride donor the complex [(indigo-*O,O'*-)Cr(II)(Cl)Cp*] could be isolated^[39] (Scheme 8), which is the only example with indigo as neutral ligand and with coordination of *cis* configured carbonyl groups. Thus, the unstable *cis*-indigo is stabilized by coordination.



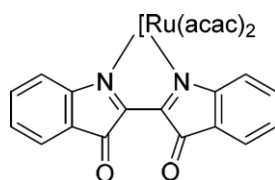
Scheme 8. A Cr^{II} complex with a neutral *cis*-indigo as *O,O* chelating ligand.

The same group of Konarev^[40] studied the reaction of reduced indigo with reduced Cp*₂IrI₂ and a diamagnetic Ir^{III} complex with *cis*-*N,N*-coordinated dianionic indigo [(*cis*-indigo-2H⁺-*N,N*)-Ir(Cp*)] was obtained. In a Cp*Ir complex containing this *cis*-*N,N*-dianionic indigo ligand and a tin(II) phthalocyanine radical anion two *cis*-*N,N*-indigo dianionic ligands are linked by a leuco *cis*-indigo dianionic ligand with strong N–O hydrogen bonding. *Cis* configuration (*O,O*-bonding) of the reduced dianion of indigo has also been detected by Konarev and co-workers in the phthalocyanine complex of titanium^{IV} [(*cis*-leuco-indigo-2H⁺-*O,O*)-Ti^{IV}(phthalocyanine²⁻)] (Scheme 9)], which was obtained by reduction of *trans*-indigo with vanadyl-phthalocyanine, using KC₈ followed by addition to a solution of TiCl₂(phthalocyanine²⁻).^[41]



Scheme 9. A Ti^{IV} complex with bis-deprotonated *cis*-leuco-indigo as *O,O*-chelate ligand.

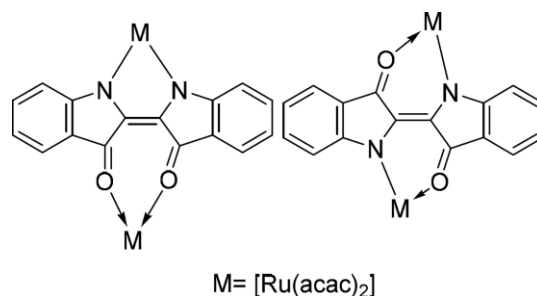
Different results have been reported for the reaction of Ru(acetylacetonate)₂ with indigo. In one communication^[34] the complexes [(Indigo-H⁺-*N,O*)-Ru^{III}(acac)₂] and [(dehydro-indigo-2H⁺-*N,N*)-Ru(acac)₂] were shown as products (Scheme 10). The paramagnetic Ru^{III} complex exhibited the usual *trans*-*N,O*-coordination of single deprotonated indigo with intramolecular N.H.O hydrogen bonding between the non-coordinated NH and carbonyl groups, whereas the second product was formulated as complex with a doubly deprotonated leuco-indigo ligand. In accordance with this formulation a longer distance was observed for the central C–C-bond in the leuco-indigo complex.



Scheme 10. Doubly deprotonated *cis*-dehydroindigo as *N,N* chelating ligand towards Ru^{II}.

Most notable, Kaim and Lahiri and their co-workers^[42] succeeded to synthesize a pair of the isomeric diruthenium com-

plexes with *trans*-*N,O,N,O* and with *cis*-*N,N,O,O* coordination of the bridging dianionic indigo ligands (Scheme 11). In the complex with *cis* configuration of the deprotonated indigo ligand a five-membered and a seven-membered chelate ring were ascertained by X-ray structure analysis. Again, the redox chemistry of these complexes with two oxidation and two reduction processes was studied.



Scheme 11. Two isomeric indigo bridged Ru^{II} complexes, showing the “normal” *N,O* chelation as well as *N,N* + *O,O* chelation.

3 Pyrrolindigo and Structural Isomers of Indigo as Ligands

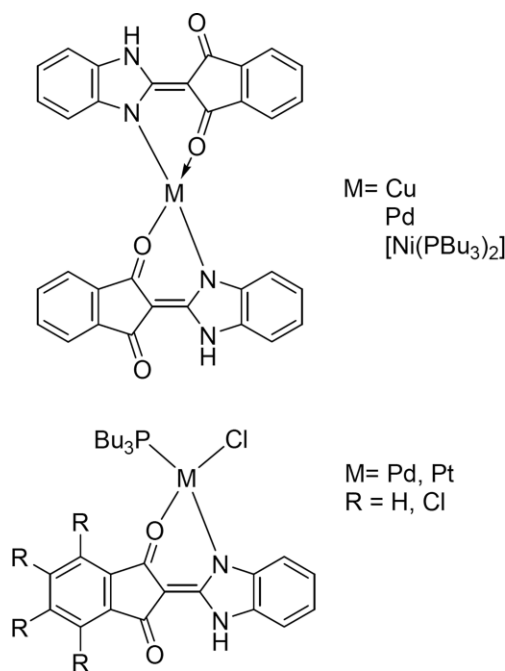
Epindolidion^[43] is a structural isomer of indigo and Lüttke and Klessinger^[44] considered it as an indigoid pigment. Several metal complexes with the dianion of epindolidion and 2,8-dimethylepindolidion could be obtained by reactions with chlorido bridged complexes [(R₃P)MCl₂]₂ (M = Pd, Pt) and [Cp*MCl]₂ (M = Rh, Ir)^[45] These bis(chelate) ligands form also deep red coordination polymers with Co^{II} and Ni^{II} salts.^[45] A related dye is triquinolobenzene^[46] and its trianion acts as tris(chelate)ligand in the structurally characterized complex [(*n*Bu₃P)(Cl)Pt]₃(triquinolobenzene-3H⁺).^[47]

From the isomers of indigo, 2-[1,3-dioxo-2-indanyline] benzimidazolines, which were prepared in 1893 in Munich by Bamberger and Berlè,^[48,49] a series of similar *N,O*-chelate complexes was accessible^[50] (Scheme 12). The heterocycles are not indigoid dyes, but the complexes thereof may be of interest – according to fundamental studies by Kaim^[51] – as potential redox active species.

In contrast to indigo and substituted indigo compounds, with pyrrolindigo always both NH-protons were exchanged by cationic metal fragments in reactions with chlorido bridged metal compounds to give indigo bridged *N,O*-chelated complexes.^[17,20] Thus the polymeric Zn^{II} and Cu^{II} chelate complexes, the pyrrolindigo bridged Pd and Pt complexes and the pentamethylcyclopentadienyl rhodium and iridium complexes could be prepared (Scheme 13). The large bathochromic shift of the absorptions in the visible region of the complexes compared to the neutral ligands is in accordance with PPP calculations.^[20]

4 Indigodiimine (“Nindigo”) as a Complex Ligand

A series of complexes have been reported with indigo diimines (“Nindigo”) as ligands, which correspond closely to



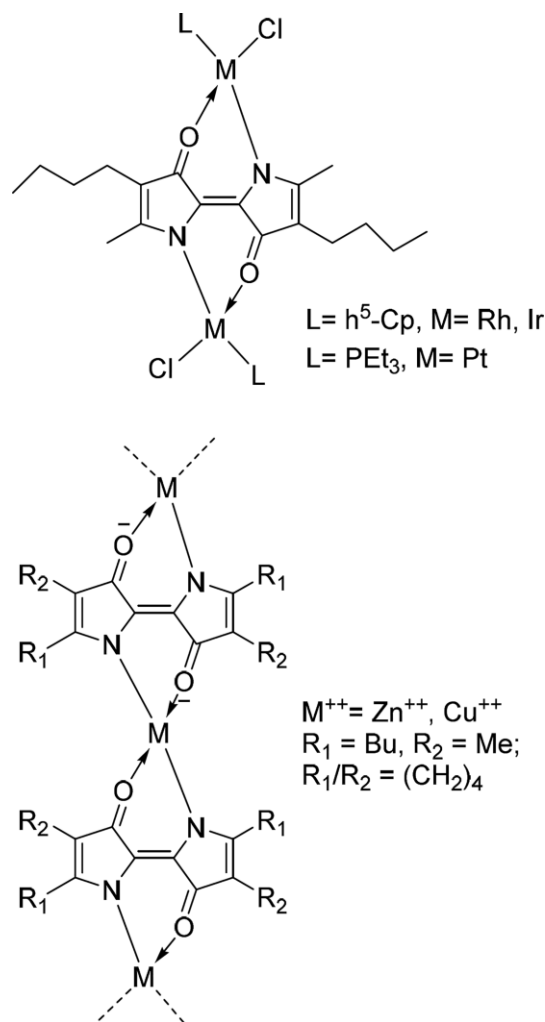
Scheme 12. 2-[1,3-Dioxo-2-indanyline]benzimidazoles as mono- N, O chelating ligands.

those with indigo itself. Hicks and co-workers^[52,53] synthesized and characterized indigo bis(arylimines) as new class of bridging ligands by reaction of indigo with aniline, TiCl₄ and 1,4-diazabicyclo[2,2,2]octane (DABCO) and could prepare a series of Nindigo bridged palladium complexes using Pd(hexafluoroacetylacetonate)₂ [Pd(hfac)₂] (Scheme 14). These complexes [(hfac)Pd(Nindigo-2H⁺)Pd(hfac)] exhibit ligand-centered redox activity and intense near infrared absorption

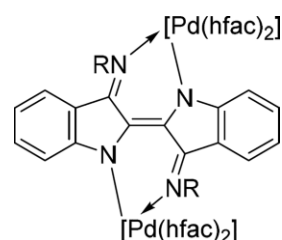
Reactions of indigo-*N,N*-diarylimines with BF₃·Et₂O give mono- or bis-BF₂-chelate complexes [(F₂B)Nindigo] or [(F₂B)Nindigo(BF₂)], which are redox active and which show intense long-wavelength absorptions near 650 and 750 nm, respectively.^[54] Reactions of the mono BF₂-Nindigo complex with Pd(hfac) gave mixed complexes with Nindigo binding both both a BF₂ and a Pd(hfac) unit^[55] (Scheme 15). Also these complexes have intense near IR absorptions and undergo multiple reversible oxidations and reductions.

One-electron oxidation or reduction of the dinuclear three-coordinate Nindigo bridged cobalt(II) complex [(Me₃Si)₂N-Co(Nindigo-2H⁺)CoN(SiMe₃)₂] [Nindigo = Indigo-bis(2,6-dimethylphenyl)imine-] generates the cation and the anionic radical of the latter complex, respectively (Scheme 16). These three complexes were characterized by X-ray structural analysis. The redox changes were proven to be indigo based. Magnetic measurement revealed, that both the cation and the anion behave as single-molecule magnets, caused by magnetic coupling of the paramagnetic salts of nindigo with the high spin Co ions (*S* = 3/2).^[56,57]

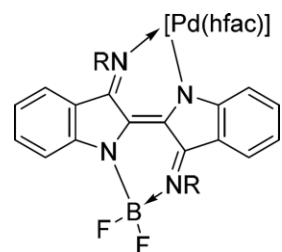
Reaction of *N,N'*-diphenylimine-indigo with Ru(acac)₂ resulted in the formation of a diruthenium complex with the nindigo bridge in the neutral leuco form [(acac)₂Ru(leuco-nin-



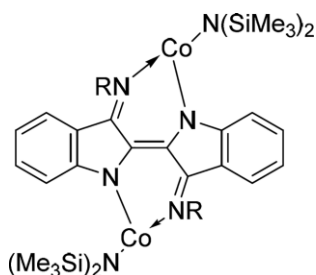
Scheme 13. Substituted pyrrolindigo as bridging bis-chelate ligand.



Scheme 14. Doubly deprotonated nindigo as bridging bis-chelating ligand.

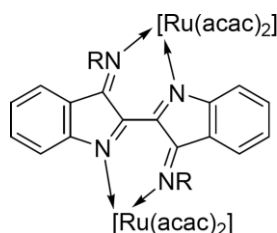


Scheme 15. Doubly deprotonated Nindigo as a ligand bridging a transition metal and a main group element.



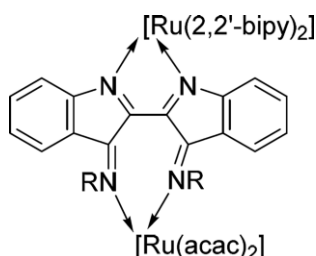
Scheme 16. A dinuclear nindigo complex, behaving as a single-molecule magnet.

digo)Ru(acac)₂] (Scheme 17). This structure is supported by the relatively long central C–C bond.^[58]



Scheme 17. Leuco-nindigo as a neutral bridging ligand.

The reaction of indigo-bis(phenyl)imine with [Ru(bipy)₂(EtOH)₂]²⁺ gave the complex with the monodeprotonated Nindigo ligand. Remarkably, in contrast to the reported complexes with *trans*-configured Nindigo ligands, reaction of the latter complex afforded with [Ru(acac)₂] a complex with *cis*-configuration of the indigo derivative, [(bipy)₂Ru(*cis*-dehydro-nindigo)Ru(acac)₂]²⁺. The Nindigo ligand obviously is neutral in this complex^[59] (Scheme 18). The complexes again are redox active.



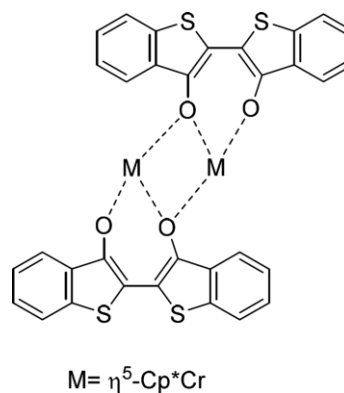
Scheme 18. *Cis*-dehydro nindigo as an unsymmetrical bridging ligand.

The parent imines of indigo, indigo-monoimine and indigo-diimine and a zinc salt of the monoimine were already reported in 1913.^[60,61] It appears of interest to study coordination of these indigo derivatives in the light of the new Nindigo complexes.

5 Thioindigo as Complex Ligand

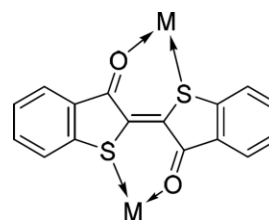
The group of Konarev succeeded to synthesize the first metal complexes of thioindigo.^[62] By reaction of bis(pentamethylcyclopentadienyl)chromium with thioindigo one Cp* ligand is substituted by a dianionic reduced thioindigo, which adopts *cis*-configuration, allowing the coordination of both carbonyl

groups to chromium. Additionally, one oxygen atom of thioindigo becomes a μ^2 -bridge to form a dimer with strong antiferromagnetic coupling of the two Cr³⁺ cations (Scheme 19). The same *O,O*-coordinated thioindigo-dianion [*cis*-thioindigo]₂ is present in a phthalocyanine indium complex, which is formed by reduction of indium(III) chloride phthalocyanine with KC₈ in the presence of cryptand-potassium and addition of thioindigo.^[41]



Scheme 19. Two thioindigo molecules acting as *O,O* chelate ligands bridged by two Cr^{III} ions.

Cis-(*O,O*)- and *trans*-(*O,S*) coordination of neutral thioindigo could be verified by Kaim and Lahiri^[63] using [Ru(acac)₂] complexes (Scheme 20).



Scheme 20. Thioindigo molecules acting as a bridging *S,O* bis-chelate ligand.

Hicks and co-workers^[64] reported the synthesis of mono and diruthenium complexes of the thioindigo-*N,N'*-diphenyldiimine, [(hfac)₂Ru(thioindigo-*N,N'*-diphenyldiimine)Ru(hfac)] and [(hfac)₂Ru(thioindigo-diimine)], which were characterized by X-ray crystallography and they emphasized the absence of thioindigo complexes. Coordination of the neutral thioindigo-imine occurs through the S and the imine N atoms.

Gompper and co-workers reported several novel derivatives of indigo and thioindigo, which may be suited as ligands in metal complexes.^[65]

It may be noted that Dube and co-workers, applied a derivative of thioindigo, hemithioindigo, for the development of a novel light driven molecular motor.^[66]

Final Remark

When the draft of this article was finished, we became aware of a very interesting article by Kaim and Lahiri on “The coordination potential of indigo, anthraquinone and related re-

dox-active dyes”.[67] In this review the redox activity and the non-innocent behavior of the indigo ligand was emphasized; in our paper we tried to cover also the historical aspects of indigo metal complexes.

Acknowledgements

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Keywords: Indigo anion; Dehydroindigo; Deprotonated reduced indigo; Indigodiimine; Thioindigo in chelate complexes

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