0.832 mmol) in pentane (20 mL) cooled to −120 °C. The resulting dark brown suspension was stirred for 48 h at −78 °C during which time it turned dark green. The NMR spectrum recorded for the dark green solution obtained after the reaction mixture had been allowed to warm to room temperature and the solvent pentane had been exchanged for C_6D_6 revealed in addition to small amounts of tBu$_3$SiH (hydrolysis product of tBu$_3$SiNa; identification by comparison with an authentic sample[5]), $R^*_2In{-}InR^*_2$ (identification by comparison with an authentic sample[4]) and **3** in a molar ratio of about 1:1. After removal of insoluble products (Cp*Na) from the original solution in pentane by filtration, removal of all volatile components under an oil pump vacuum (tBu$_3$SiH, pentane), and dissolution of the dark green residue in benzene (10 mL), **3** (0.072 g, 0.034 mmol, 32 %) crystallized as dark green parallelpipeds in the course of 7 d at room temperature. ^{1}H NMR (C_6D_6, TMS internal): $\delta = 1.362$ (s; 6 SitBu$_3$); ^{13}C{^{1}H} NMR (C_6D_6, TMS internal): $\delta = 29.29/33.09$ (18 *C*Me$_3$/18 C*Me*$_3$); ^{29}Si NMR (C_6D_6, TMS external): $\delta = 80.95$ (6 SitBu$_3$).

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[1] N. Wiberg, T. Blank, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 887; *Angew. Chem. Int. Ed.* **1999**, *38*, 839, and references therein.

[2] Crystal structure analysis of **3**: STOE-IPDS diffractometer, $Mo_{K\alpha}$ irradiation, measurement temperature 200(2) K. The crystal was mounted in perfluoropolyether. Crystal dimensions: $0.5 \times 0.4 \times 0.2$ mm^3, monoclinic, space group $C2/c$ with $a = 24.657(5)$, $b = 16.648(3)$, $c = 27.798(6)$ Å, $\beta = 115.50(3)°$, $V = 10299(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.465$ Mg m^{-3}, $\mu = 1.863$ mm^{-1}, $\theta = 3.84 - 51.84°$, $-30 \leq h \leq 30$, $-20 \leq k \leq 20$, $-34 \leq l \leq 33$, 9911 measured reflections, of which 9911 independent; 6929 with $I > 4\sigma(I_0)$ included in the refinement, numerical absorption correction by local scaling (transmission: max. 0.8202, min. 0.6404), $R1 = 0.0293$, $wR2 = 0.0881$, GOOF 0.916, no restraints, 469 parameters, residual electron density: max. 1.218, min. −0.728 e Å^{-3}. The structure was solved by direct methods and refined against F^2 for all observed reflections (structure solution with SHELXS 94, refinement with SHELXL 93). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114210. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[3] The structural formula indicates several types of supersilyl groups for the compound which is only sparingly soluble at room temperature and almost insoluble at lower temperatures in organic media. Thus, **3** possibly behaves in a fluctional manner in solution.

[4] N. Wiberg, K. Amelunxen, H. Nöth, M. Schmidt, H. Schwenk, *Angew. Chem.* **1996**, *108*, 110; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 65.

[5] N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217.

[6] Nothing definitive can be said about the mechanism of the formation of **3** from Cp*In and R*Na in pentane. However, initially the Cp* group is replaced by a supersilyl group, resulting in R*In and NaCp*. The monomeric supersilylindium could then be converted into the tetrahedrane $R^*_4In_4$ **1c** via $R^*_2In_2$ and the former could then dimerize with elimination of supersilyl groups to give the octaindane $R^*_6In_8$ (**3**). The supersilyl groups eliminated could react with R*In to give the indanyl R^*_2In and this then subsequently gives the diindane $R^*_4In_2$.

[7] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; see also R. W. Rudolph, *Acc. Chem. Res.* **1976**, *9*, 446, as well as R. E. Williams, *Adv. Inorg. Chem. Radiochem.* **1976**, *18,* 67.

[8] D. M. P. Mingos, *Nature* **1972**, *236*, 99; D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311; see also M. McPartlin, *Polyhedron* **1984**, *3*, 1279.

[9] Accordingly, $R^*_6In_8$ (**3**) cannot be described as a supersilyl derivative of the *closo*-indate $In_8H_8{}^{2-}$, a homologue of the isolable *closo*-borate $B_8H_8{}^{2-}$, lacking two hydride ions.

[10] Turbomole program: E. Eichhorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; SVP basis sets: A. Schäfer, H. Horn, R. Ahlrichs, *Z. Phys. Chem.* **1992**, *97*, 2751.

[11] The computer-intensive studies (230 atoms!) could not be shortened either by symmetry restrictions (e.g. D_{3d}) or by the use of smaller ligands (transfer to In_8H_6) (in the second case structures are obtained with bridging hydrogen atoms).

[12] N. Wiberg, H.-W. Lerner, H. Nöth, W. Ponikwar, *Angew. Chem.* **1999**, *111*, 1176; *Angew. Chem. Int. Ed.* **1999**, *38*, 1103, and references therein.

Terthienyl-Based Redox-Switchable Hemilabile Ligands: Transition Metal Polymeric Complexes with Electrochemically Tunable or Switchable Coordination Environments?**

Dana A. Weinberger, Thomas B. Higgins,
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Herein we report the synthesis and characterization of the first transition metal complexes (**4a,b**) formed from redox-switchable terthienyl-based hemilabile ligands (**1a,b**) (Scheme 1). These ligands were designed to possess several key features. First, they are hemilabile when bound to Ru^{II} centers in a κ^2 fashion by virtue of their phosphane and terthienyl moieties.[1] Second, the redox-active terthienyl group in **4b** can be electrochemically polymerized at an oxidation potential lower than that of the Ru^{II} centers, allowing the generation of an electroactive film of poly-**4b** with the metal centers still intact. Terthienyl-based polymers can be reversibly oxidized, thereby providing electrochemical control over the binding constant of the polymeric ligand in poly-**4b** for transition metal centers dispersed along its thienyl backbone. Although others have grafted metal centers onto the backbone of preformed conducting polymers to form substitutionally inert linkages[2a,b] or polymerized metal-containing monomers,[2c–h] **4b** is the first isolable, polymerizable monomer suitable for forming a polymeric metal ligand

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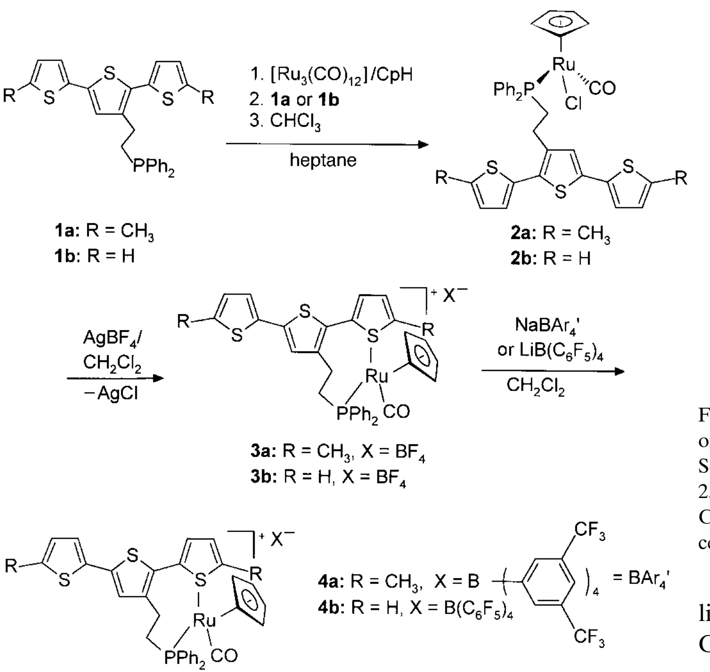

Scheme 1. Schematic diagram of the synthesis of metal complexes **4a,b**. Cp = cyclopentadienyl.

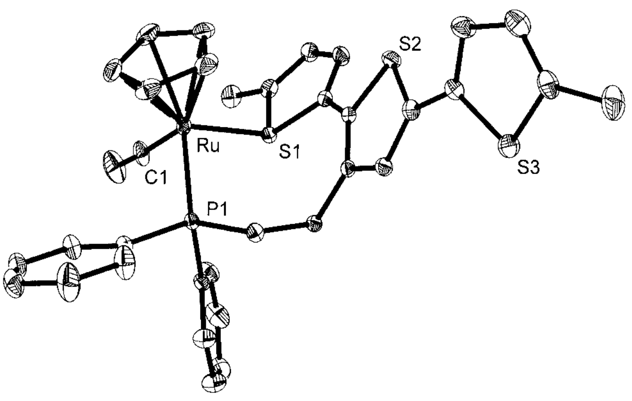

Figure 1. ORTEP diagram of **4a** (counterion and hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability). Selected bond lengths [Å] and bond angles [°]: Ru–C$_{cent}$ 1.894(4), Ru–S1 2.3903(9), Ru–P1 2.3424(9), Ru–C1 1.889(4); S1-Ru-P1 92.40(3), P1-Ru-C1 91.00(13), C1-Ru-C$_{cent}$ 124.0(2); C$_{cent}$-Ru-S1 122.5(12); C$_{cent}$ = ring centroid of Cp ring.

complex with an electrochemically controllable coordination center. Although the concept of a "redox-switchable hemilabile ligand (RHL)" for electrochemically controlling transition metal reactivity is now well established,[3] previous studies have focused almost exclusively on metallocene moieties as the redox-active group that provides control over ligand lability. Therefore, poly-**4b** and non-polymerizable, methyl-capped model complex **4a** give entry into a new class of terthienyl-based RHLs and provide an initial opportunity to study this class of ligand in the context of a conducting polymer.

Complexes **2a,b** were synthesized from the new ligands **1a,b** by a modification of literature procedures[4] for synthesizing analogous, isoelectronic complexes (see Supporting Information) (Scheme 1). Compounds **3a,b** were prepared by stirring **2a,b** in CH$_2$Cl$_2$ with AgBF$_4$ at room temperature. The B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$ and B(C$_6$F$_5$)$_4$ salts (**4a,b**) were prepared from **3a,b** by metathesis with appropriate alkali metal salts (Scheme 1). Each salt has advantages with respect to crystallization, solubility, or spectroelectrochemistry, and thus the use of a particular salt reflects the best balance of these properties. The solution spectroscopic data for **3a,b** and **4a,b** are consistent with their proposed structures. In addition, an X-ray diffraction study performed on a single crystal of **4a**[5] shows that in the solid state the thienyl ring closest to the methylene group is bound to the Ru^{II} center in an η^1-fashion and that the absolute diastereomeric configuration of the complex is Ru$_R$S$_S$/Ru$_S$S$_R$[6] (Figure 1). Although η^1-[1, 7c,d] and η^5-thienyl[7c,d] and η^5-terthienyl[7a,b] complexes have been reported, this is the first structurally characterized η^1-terthienyl metal complex.

We have used a methyl-capped complex, **4a**, to determine the maximum "RHL effect" or thermodynamic perturbation one can expect for this class of compound as a function of ligand-centered oxidation. The cyclic voltammetry of **4a** in CH$_2$Cl$_2$/0.1 M NaBAr$'_4$ exhibits a chemically reversible, one-electron, terthienyl-based oxidation/reduction wave at $E_{1/2}$ = 735 mV vs. FcH/FcH$^+$ (confirmed by rotating disk electrode experiments, see Supporting Information) followed by an irreversible, Ru-centered oxidation at 1180 mV. The assignment is based upon the observation that a model complex, [Cp(CO){P(CH$_2$CH$_3$)Ph$_2$}Ru(CH$_3$CN)]BF$_4$, which does not possess a terthienyl ligand is irreversibly oxidized at 1270 mV vs. FcH/FcH$^+$ in 1/1 CH$_3$CN/CH$_2$Cl$_2$. Significantly, if CH$_3$CN (4 equiv) is added to **4a**, the complex is converted to a CH$_3$CN adduct [Cp(CH$_3$CN)RuCO{3′-(2-diphenylphosphinoethyl)-5,5″-dimethyl-2,2′: 5′,2″-terthiophene}]B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$ (**5**) by displacement of the η^1-terthienyl moiety from the Ru center. The $E_{1/2}$ of **5** is 535 mV vs. FcH/FcH$^+$ and allows one to *quantify* the increase in Ru^{II} binding constant (K) for CH$_3$CN upon oxidation of the terthienyl ligand ($\Delta E_{1/2} = (RT/nF)\ln(K_{ox}/K_{red})$; $K_{ox}/K_{red} = 2 \times 10^3$). Alternatively, this ratio may be viewed as an inverse measure of the decrease in Ru^{II}-terthienyl RHL binding constant that accompanies ligand-based oxidation.

Spectroelectrochemical FT-IR experiments of **4a** in CH$_2$Cl$_2$/0.1 M NaBAr$'_4$ provide insight into the influence of terthienyl oxidation state on the electronic properties of the bound Ru^{II} center. Terthienyl-centered oxidation/reduction of **4a** results in a reversible increase in its CO stretching frequency of 19 cm^{-1} (from 1992 to 2011 cm^{-1} in IR *difference* spectrum) (Figure 2). The magnitude of this shift is substantial considering that direct spectroelectrochemical oxidation of the Ru^{II} center in [Cp(CO){P(CH$_2$CH$_3$)Ph$_2$}RuCl] results in a 90 cm^{-1} shift in $\tilde{\nu}_{CO}$ ($\tilde{\nu}_{CO}$: [Ru^{II}] = 1955 cm^{-1}; [Ru^{III}] = 2045 cm^{-1}), suggesting that terthienyl-based oxidation in **4a** is worth approximately 1/5 of an electron at the Ru center in terms of electronic change.

Poly-**4b** has been electrochemically deposited onto an Au electrode by electrochemically oxidizing **4b** in CH$_2$Cl$_2$/0.1 M LiB(C$_6$F$_5$)$_4$. The characteristic oxidative polymerization wave for this terthienyl compound is observed at 765 mV vs. FcH/FcH$^+$, and the reversible oxidation/reduction wave for a typical deposited polymer is $E_{1/2}$ = 540 mV vs. FcH/FcH$^+$.

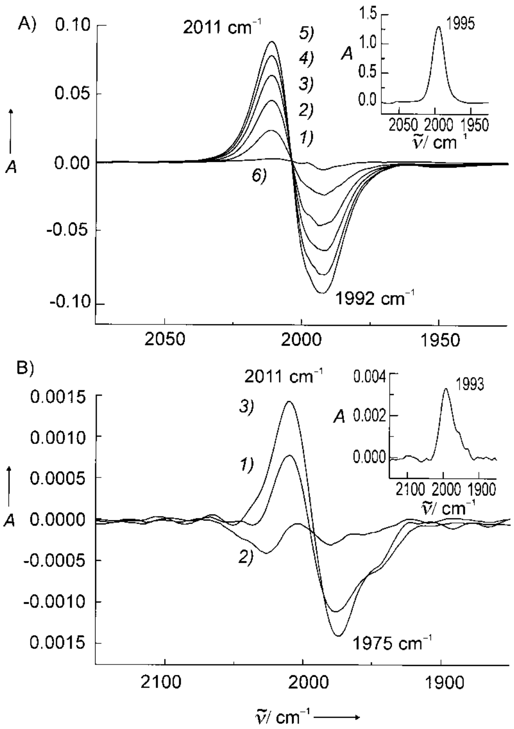

Figure 2. Spectroelectrochemical (FT-IR) experiments. A): $0.01\,\text{M}$ **4a**, $0.1\,\text{M}$ $NaBAr'_4$, CH_2Cl_2. Time elapsed difference spectra of **4a** after its oxidation with an Au working electrode held at 600 mV vs. Ag wire; the growth of the oxidized complex **4a**$^+$ is evidenced by the growth of the band at 2011 and concomitant decrease of the band at 1992 cm^{-1}. Difference spectra are obtained by subtracting the initial spectrum of **4a** from the spectrum of **4a** recorded after being held at 600 mV for: 1 min (*1*), 3 min (*2*), 5 min (*3*), 7 min (*4*), and 9 min (*5*); FT-IR difference spectrum after completion of the experiment and after holding the electrode at 0 V for 28 min (*6*). Almost quantitative reformation of **4a** is effected. Inset: FT-IR spectrum of complex **4a** ($\tilde{\nu}_{CO} = 1995$ cm^{-1}). B): FT-IR difference spectra of poly-**4b** on an Au thin film electrode as function of oxidation. Difference spectra are obtained by subtracting the initial spectrum of poly-**4b** from the spectrum of poly-**4b** recorded at a desired potential for a specified period of time. Film oxidized at 1200 mV vs. $Ag/AgNO_3$ for 1 min (*1*), at 0 mV for 1 min, showing return of film to its unoxidized state (*2*), and at 1200 mV for 1 min (*3*). Note: although the difference band for the polymer (1975 cm^{-1}) differs from that of the monomer (1992 cm^{-1}), this change has been attributed to inhomogeneity within the polymeric films. Inset: FT-IR spectrum of poly-**4b** ($\tilde{\nu}_{CO} = 1993$ cm^{-1}).

Specular reflectance FT-IR spectroscopy, energy dispersive spectroscopy (EDS), and reactivity studies have been performed on the resulting polymers to confirm that the basic monomer fragment does not degrade during polymerization. For example, the FT-IR spectrum of poly-**4b** exhibits a single metal carbonyl band at 1993 cm^{-1}, which is almost identical in frequency to that of the monomer (1995 cm^{-1}). EDS shows within experimental error that the Ru:S ratio remains constant before and after polymerization, suggesting that all of the metal sites remain intact (i.e. no leaching occurs, see Supporting Information). Due to its insolubility, the average molecular weight of the polymer has not been determined. Evidence that the poly-terthienyl backbone in poly-**4b** can dissociate from the Ru centers was obtained by studying the reactivity of poly-**4b** with *tert*-butylisocyanide. When poly-**4b** is immersed in a $0.04\,\text{M}$ solution of $(CH_3)_3CNC$ in CH_2Cl_2, the resulting film exhibits a new IR band at 2175 cm^{-1} in the metal isocyanide region of the spectrum. This band matches that assigned to the isocyanide stretch in $[Cp\{(CH_3)_3CNC\}RuCO\{3'\text{-(2-diphenylphosphinoethyl)-2,2}':5',2''\text{-terthiophene}\}]BF_4$ (**6**), formed upon reaction of **3a** and *t*BuNC (2175 cm^{-1}).

Although methyl-capped **4a** has only two stable electrochemically accessible oxidation states, poly-**4b** potentially has many due to the terthienyl repeat unit along the backbone. Significantly, spectroelectrochemical (FT-IR) experiments performed on poly-**4b** show a decrease in the metal carbonyl *difference* band at 1993 cm^{-1} upon oxidation and a concomitant increase in a new *difference* band at 2011 cm^{-1} (Figure 2B). This process, which can be electrochemically reversed, further confirms that the polyterthienyl backbone is coordinated to and in electronic communication with the Ru centers. Moreover, the spectroscopy is a measure of the electronic perturbation at the Ru centers, which is significant and compares quite well with the spectroscopy for model complex **4a**. Although several groups have suggested that metal-conducting polymer complexes might give access to systems with tunable electrochemical properties based on extent of oxidation,[2a] we do not observe gradual shifts in CO stretching frequency to higher energy with poly-**4b** as it is oxidized. Instead, only one quantized shift is observed with continued growth of the *difference* band at 2011 cm^{-1} as the polymer is oxidized. It seems that the charged Ru fragment causes the electron holes produced during oxidation of the polymer backbone to remain localized on the uncomplexed thienyl rings, at least on the timescale of the IR experiment. Thus, upon oxidation of poly-**4b**, the maximum spectroelectrochemical shift is observed, consistent with that observed for model complex **4a**. This type of effect, although not tuning, can be quite useful for modulating polymer metal complex binding constants. Future work will focus on studying the small molecule uptake and release properties of these novel polymers as a function of polymer oxidation state.

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[1] a) J. W. Benson, R. J. Angelici, *Organometallics* **1992**, *11*, 922; b) J. W. Benson, R. J. Angelici, *Organometallics* **1993**, *12*, 680.

[2] a) M. O. Wolf, M. S. Wrighton, *Chem. Mater.* **1994**, *6*, 1526; b) A. Shaver, I. A. Butler, J. P. Gao, *Organometallics* **1989**, *8*, 2079; c) T. B. Higgins, C. A. Mirkin, *Chem. Mater.* **1998**, *10*, 1589; d) T. B. Higgins, C. A. Mirkin, *Inorg. Chim. Acta* **1995**, *240*, 347; e) J. L. Reddinger, J. R. Reynolds, *Chem. Mater.* **1998**, *10*, 1236; f) K. F. Martin, T. W. Hanks, *Organometallics* **1997**, *16*, 4857; g) K. Martin, M. Dotson, M. Litterer, T. W. Hanks, C. Veas, *Synth. Met.* **1996**, *78*, 161; h) S. S. Zhu, P. J Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1996**, *118*, 8713.

[3] a) A. M. Allgeier, C. S. Slone, C. A. Mirkin, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 550; b) C. S. Slone, C. A. Mirkin, G. P. A. Yap, I. A. Guzei, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 10743; c) C. A. Sassano, C. A. Mirkin, *J. Am. Chem. Soc.* **1995**, *117*, 11379; d) E. T. Singewald, C. A. Mirkin, C. L. Stern, *Angew. Chem.* **1995**, *107*, 1725; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1624; e) A. M. Allgeier, E. T. Singewald, C. A. Mirkin, C. L. Stern, *Organometallics* **1994**, *13*, 2928.

[4] A. P. Humphries, S. A. R. Knox, *J. Chem. Soc. Dalton Trans.* **1975**, 1710.

[5] Crystal data for $C_{66}H_{42}BF_{24}OPRuS_3$ (**4a**): triclinic, $P\bar{1}$, $a = 13.2861(3)$, $b = 15.4088(2)$, $c = 17.4920(3)$ Å, $\alpha = 103.8463(2)$, $\beta = 94.7346(7)$, $\gamma = 110.1334(8)^\circ$, $V = 3306.33(12)$ Å^3, $Z = 2$, $T = 198(2)$ K, $\rho_{calcd} = 1.553$ g cm^{-3}, $R(F) = 0.0514$ for 9428 observed independent reflections ($4^\circ \leq 2\theta \leq 57^\circ$). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410356.

[6] Ligand priority order: Ru (C_5H_5 > thiophene > phosphane > CO); S (Ru, C-thiophene, C–CH_3, lone pair), see K. Stanley, M. C. Baird, *J. Am. Chem. Soc.* **1975**, *97*, 6598.

[7] a) D. D. Graf, K. R. Mann, *Inorg. Chem.* **1997**, *36*, 150; b) D. D. Graf, N. C. Day, K. R. Mann, *Inorg. Chem.* **1995**, *34*, 1562. For reviews of thiophene coordination: c) T. B. Rauchfuss, *Prog. Inorg. Chem.* **1991**, *39*, 259–329; d) R. J. Angelici, *Coord. Chem. Rev.* **1990**, *105*, 61.

4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl]-benzoic Acid: A Novel Efficient and Selective Iron(III) Complexing Agent**

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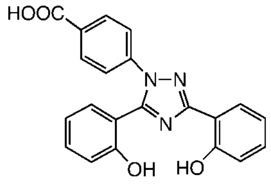
Bernard Faller, René Lattmann, and
Hans Peter Schnebli

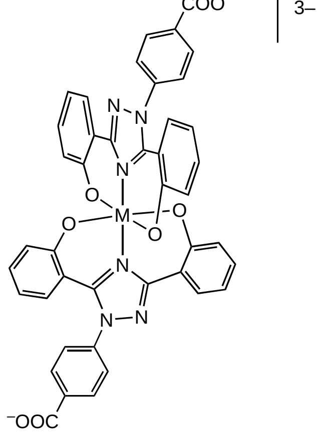
Clinical medicine recognizes several diseases which are due to defects in iron homeostasis.[1] Iron deficiency anaemia is rather common but can be treated easily. By comparison, iron overload is relatively rare but is associated with more severe morbidity. Since man is unable to actively excrete iron, excess iron, once taken up, deposits in tissues in the form of solid FeOOH which then can lead to organ damage and ultimately death. Frequent blood transfusions, as are necessary in the treatment of haematological defects such as β-thalassaemia major (more than 500 000 patients world-wide), are a well recognized cause of iron overload.[2] Therapeutically useful chelators can complex excess tissue Fe^{III}, thus transforming it into a soluble, excretable form. Currently, the siderophore desferrioxamine-B (Desferal) is by far the clinically most widely used chelator. However, this compound has a very short biological half-life and, in addition, cannot be administered orally. Because of this, there has evolved an intensive search for new iron chelators in recent years.[3] Clearly, in addition to low toxicity, appropriate tissue distribution and pharmacokinetics, the metal-binding properties, for example high stability of the Fe^{III} complexes, and high selectivity with respect to other biologically important metals of such compounds will be of central importance.

We herein report on the metal complexing properties of a substituted 3,5-bis(*ortho*-hydroxyphenyl)-1,2,4-triazole in solution. Ryabukhin had already discovered that compounds of this class tend to form complexes with divalent transition metal ions in the form of insoluble polymers.[4] Our studies have shown that the corresponding benzoic acid H_3L[5] exhibits ideal properties for use in the treatment of iron overload. Owing to the good oral bioavailability, tolerance in animal studies, and efficient excretion of iron, this ligand is a possible successor to Desferal.[6]



H_3L

Free H_3L reacts in solution as a weak, triprotic acid, and in the neutral pH range it is present as the carboxylate ion H_2L^-. The nitrogen atoms of the five-membered heterocycle cannot be protonated above pH 2. With Fe^{III} this ligand forms a dark violet 1:1 complex and a deep red 1:2 complex.[7] The peripheral carboxylate group does not participate in the metal-complex formation; [FeL] can therefore be protonated once, and $[FeL_2]^{3-}$ can be protonated twice. In accord with the negative charge $[FeL_2]^{3-}$ is the slightly stronger base. Thus L^{3-} acts as a tridentate meridionally coordinating ligand,[8] where binding of the metal center occurs through the two phenolate groups and one of the nitrogen atoms of the heterocycle. Consequently, the bis complex $[FeL_2]^{3-}$ adopts a *trans*-N_2O_4 coordination. With Al^{III} complex formation is so slow that separate signals for the free ligand, the 1:1 complex, and the 1:2 complex are observable in the ^1H NMR spectrum.[9] The individual protonation equilibria, however, exhibit time-averaged signals with pD-dependent shifts. According to these NMR spectroscopic studies, free H_3L is exclusively present below pD 2. In the range $2 < pD < 4$ $[Al(HL)]^+$ is formed, which is subsequently deprotonated to [AlL]. The formation of 1:2 complexes begins above pD 5.5, and at higher pH the 1:1 complex disappears completely. The NMR spectra for the 1:2 complexes show only ten signals for the aromatic protons. Apparently the two ligands are symmetry-equivalent (C_2), which is consistent with the structure proposed for $[ML_2]^{3-}$. In strongly alkaline solutions the complex decomposes to form $[Al(OH)_4]^-$, and in 5 mol dm^{-3} NaOD only the signals of free, deprotonated L^{3-} are observed.



$[ML_2]^{3-}$ (M = Al, Fe)

The various protonation and complex formation equilibria could be elucidated quantitatively by extensive potentiometric and spectrophotometric meas-

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