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Chelate complexes of cobalt(III) with bis(dithiolate) ligands: backbone influence on the electronic properties and the reactivity of the metal center

Wolfram W. Seidel and F. Ekkehardt Hahn *

Anorganisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

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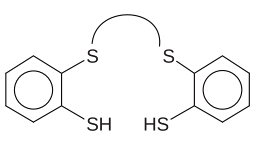
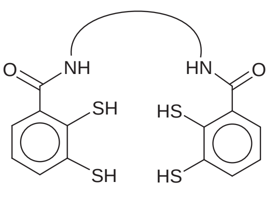
The tetradentate bis(dithiolate) ligands 1,4-bis[(2,3-disulfanylbenzamido)methyl]benzene H_4L^1 and 1,7-bis(2,3-disulfanylbenzamido)heptane H_4L^2 were prepared and converted into the dinuclear titanocene complexes $[(TiCp_2)_2(L^1)]$ **1** and $[(TiCp_2)_2(L^2)]$ **2**, respectively. A ligand transfer reaction of **1** and **2** with $[NR_4]_2[CoCl_4]$ (R = Et or Me) led to the formation of the bis(dithiolato)cobaltate(III) complexes $[NEt_4][Co(L^1)]$ **3** and $[NR_4][Co(L^2)]$ (R = Et **4a** or Me **4b**). The anion $[Co(L^2)]^-$ adopts an approximately square-planar co-ordination geometry. Two anions are connected by intermolecular Co–S contacts at the apical position of the metal to form $[Co(L^2)]_2^{2-}$. In contrast, mononuclear **3** turned out to be unstable with respect to its co-ordination polymer. This phenomenological difference between **3** and **4a**, **4b** is reflected in the UV-VIS and cyclic voltammetry data of the complexes, which are compared to the data of the corresponding prototype complex tetraethylammonium [bis(3-*N*-benzylcarbamoylbenzene-1,2-dithiolato)cobaltate(III)] **5** with two unbridged dithiolato-ligands $(L^3)^{2-}$.

Polythiolate chelate ligands are able to force either unusual co-ordination geometries[1] or to effect subtle changes in the complex geometry[2] due to the steric demand of the ligand backbone. These structural changes often cause desirable consequences for the electronic properties[1] as well as for the reactivity at the metal center.[1,2] By comparison of such complexes with their prototypes[3] exhibiting unbridged thiolates, structure behaviour relationships can be inferred, which eventually are expected to shed light on structure function relationships in certain metalloenzymes with sulfur dominated co-ordination in a cofactor.

Multidentate, sulfur-rich ligands of type **A** based on benzene-1,2-dithiol have been used successfully in the preparation of model compounds for the active sites in nitrogenase[4] and for certain nickel enzymes.[5] In these ligands two aromatic dithiolate units are bridged *via* a thioether link which leads to a tetradentate ligand with two thiolate and two thioether sulfur donor atoms. The thioether links lead, in spite of the superb properties of ligands of type **A**, to a loss of the dithiolene character in the bidentate binding unit.



A



B

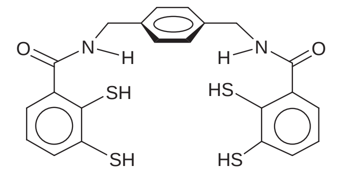
Our approach to sulfur-rich multidentate ligands was directed at the utilization of the dithiolene-like metal binding capacity of benzene-1,2-dithiolates, that differs from the benzene thiolate-thioether arrangement in **A**. We synthesized tetradentate ligands with two benzene-1,2-dithiolate donors of type **B** in which the bidentate binding unit might retain some dithiolene character upon co-ordination. Our research was particularly prompted by the intriguing "non innocent" behaviour of dithiolene ligands[6] including the stability of their complexes in two or more oxidation states and the (minor[7] or major[8]) dependence of the complex co-ordination geometry on the oxidation state of the metal. The geometry of $[Mn(tdt)_2]^{n-}$ (tdt^{2-} = toluene-3,4-dithiolate) for instance changes from planar ($n = 1$) to distorted tetrahedral ($n = 2$) upon reduction.[8] A suitably bridged bis(dithiolate) ligand of type **B** might not be able to accommodate both co-ordination geometries and thus can destabilize a specific oxidation state possibly generating an unprecedented reactivity. Thus, ligands of type **B** offer not only the opportunity for the preparation of new model complexes for the active sites in sulfur containing metalloenzymes but might also allow an investigation of how geometric constraints originating comparatively far from the metal centre in the organic backbone of the ligand affect the properties of the co-ordinated metal centre.

A first report on the synthesis and co-ordination chemistry of a tripodal tris(dithiolate) ligand appeared in 1995.[9] A report on a bis(dithiolate) ligand and its chelate complex with the CpTi fragment was published recently.[10] In this contribution we report on cobalt(III) complexes of the bis(dithiolate) ligands H_4L^1 and H_4L^2. We describe the synthesis of the complex anions $[Co(L^1)]^-$ and $[Co(L^2)]^-$ by a dithiolate transfer reaction as well as the prototype complex with an unbridged dithiolate ligand $[Co(L^3)_2]^-$. In addition, a comparison of the UV-VIS and cyclic voltammetry data of all bis(dithiolato)cobaltate complexes is presented.

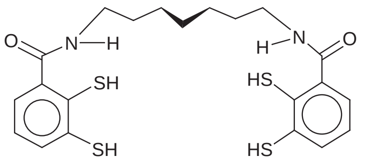
Results and discussion

Preparation of the complexes

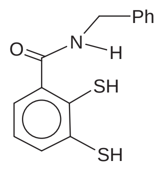
The investigation of the co-ordination chemistry of H_4L^1 and H_4L^2 has been hampered by the poor solubility of these ligands in most organic solvents (exceptions dmf and dmso). In addition, the sensitivity of the thiol functions to aerial oxidation restricted possible purification methods for them. The solubility in protic solvents can be improved considerably upon complete deprotonation with NaOMe. However, simple metathesis reactions of Na_4L^1 or Na_4L^2 with metal halides like $MCl_2(H_2O)_6$ (M = Ni or Co) proved unsuccessful at least in our hands,



H_4L^1



H_4L^2



H_2L^3

apparently because the high reactivity of these salts promotes the formation of polynuclear species.

In contrast, we found that ligand transfer reactions utilizing the halophilicity of the Cp_2Ti unit constitutes a useful tool for the synthesis of chelate complexes with H_4L^1 and H_4L^2. The dinuclear bis(titanocene) complexes of $(L^1)^{4-}$ and $(L^2)^{4-}$ are easily accessible by reaction of $[TiCp_2Cl_2]$ with H_4L^1 and H_4L^2 and triethylamine in thf. The intensly green complexes $[(TiCp_2)_2(L^1)]$ **1** and $[(TiCp_2)_2(L^2)]$ **2** are air stable and highly soluble in aprotic solvents like thf and CH_2Cl_2. In addition, they can be subjected to chromatographic purification. This advantage turned out to be crucial due to the restricted opportunities to purify unco-ordinated H_4L^1 or H_4L^2.

In our previous work[9,10] we found complex **1** to be reactive towards certain inorganic halides like HCl and NR_4Cl. The halophilicity of the Cp_2Ti unit has been exploited previously in transmetallation reactions between titanocene dithiolate complexes and late transition metal halides to give dithiolate complexes of the late transition metals and $[TiCp_2Cl_2]$.[11] This type of transfer has also been extensively demonstrated with non-metal halides, which allowed for the preparation of cyclic sulfur derivatives from $[TiCp_2S_5]$ and S_xCl_2.[12] We decided to investigate the straightforward reaction of **1** and **2** with tetrachlorometalates invoking the simultaneous transfer of two dithiolate units. A CH_3CN–thf solvent mixture had to be used to keep both the salts $[NR_4]_2[CoCl_4]$ and the uncharged complexes **1** or **2** in solution. Whereas at ambient temperature no reaction could be observed, under reflux conditions a slow change over the course of hours from dark green towards eventual intense blue indicated the formation of bis(dithiolato)-cobaltate(III) complexes.[13] Thus, $[NR_4]_2[CoCl_4]$ and **1** or **2** reacted under elimination of two equivalents of $[TiCp_2Cl_2]$ and aerial cobalt(II) oxidation to yield $[NEt_4][Co(L^1)]$ **3** and $[NR_4][Co(L^2)]$ (R = ethyl **4a** or methyl **4b**), respectively (Scheme 1). Both the solubility of **3** and **4a**, **4b** in thf, CH_2Cl_2 and CH_3CN and the detection of the parent anions in the FAB mass spectra are in accord with the assumption of mononuclear chelate complexes for **3** and **4a**, **4b**. Both salts containing the $[Co(L^2)]^-$ complex anion could be crystallized by either diffusion of Et_2O in a CH_3CN solution (**4a**) or by cooling of a toluene–acetone solution from 50 °C to ambient temperature (**4b**).

The determination of the molecular structure of complex **4b** by X-ray diffraction was hampered by the small size of the thin, needle shaped crystals. The results obtained from three independent data sets are unsufficient for publication but they confirm the identity of **4b** as chelate complex containing the two dithiolate binding units of $(L^2)^{4-}$. A number of structure determinations of bis(benzenedithiolato)cobaltate(III) complexes have been published.[14–16] The complex anions $[Co(tdt)_2]^-$ [14] and $[Co(S_2C_6Cl_4)_2]^-$ [15] exhibit an approximately square-planar co-ordination geometry with Co–S distances of 2.15–2.20 Å and they share this feature with the $[Co(L^2)]^-$ anion. Moreover, two molecules of $[Co(L^2)]^-$ are connected by cobalt–sulfur contacts. Remarkably, $[Co(S_2C_6Cl_4)_2]^-$ shows the same structural characteristics, whereas mononuclear $[Co(tdt)_2]^-$ does not. Apparently the electron poorer nature of $(L^2)^{4-}$ and $C_6Cl_4S_2^{2-}$ compared to tdt^{2-} enhances the electrophilicity at the cobalt centre thereby leading to the increase of the co-ordination number in the solid state.

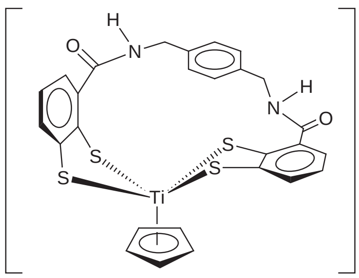
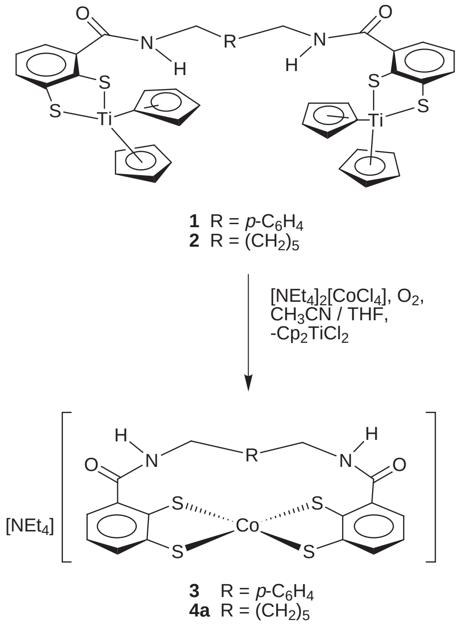


Fig. 1 Molecular structure of the anion in $[NMe_4][TiCp(L^1)]$.



Scheme 1 Synthesis of the complexes **3** and **4a**.

Reactivity of complex 3

Solutions of complexes **4a** and **4b** in aprotic solvents can be kept without any sign of decomposition. Surprisingly, dark blue solutions of **3** in CH_2Cl_2 or CH_3CN decolourize over the course of days with irreversible precipitation of a blue solid. Microanalytical and UV-VIS spectroscopic data (in dmf, see below) of this secondary product **3*** are identical to those calculated for **3**, which led us to the assumption of a polymeric structure for **3***. We assume, that a gradual conversion of the chelate complex anion $[Co(L^1)]^-$ into a complex polymer by way of a chelate ring opening polymerization takes place. This would lessen the strain in the small backbone of the complex anion $[Co(L^1)]^-$. This assumption is corroborated by inspection of the structural parameters of $[NMe_4][TiCp(L^1)]$, the only other known complex of the $(L^1)^{4-}$ ligand.[10]

The $[TiCp(L^1)]^-$ anion shows bent chelate rings in an *exo*/*endo* fashion (Fig. 1). This *exo*/*endo* bend reduces the mutual distance of the amide groups to be bridged and allows the amide functions to assume the favored twist out of the aromatic planes. This form of strain reduction is unlikely for complex **3**, because bent chelate rings are so far unknown for bis(dithiolato)-cobaltate(III) complexes. A dinuclear species with cobalt sulfur contacts between the CoS_4 planes as observed in the solid state structure of **4b** could be considered as a

Table 1 UV-VIS Data[a] of bis(benzenedithiolato)cobaltate(III) complexes

Complex	λ_1/nm	λ_2/nm	λ_3/nm
3 $[NEt_4][Co(L^1)]$[b]	320 (−)	363 (−)	653 (−)
4a $[NEt_4][Co(L^2)]$[b]	325 (11200)	368 (11400)	660 (6500)
5 $[NEt_4][Co(L^3)_2]$[b]	323 (10700)	367 (11100)	653 (6300)
$[NBu_4][Co(tdt)_2]$[13,c]	315 (12700)	361 (13700)	660 (12000)

[a] Values in parentheses: ε/M^{-1} cm^{-1}. [b] Solvent CH_2Cl_2. [c] Solvent CH_3CN.

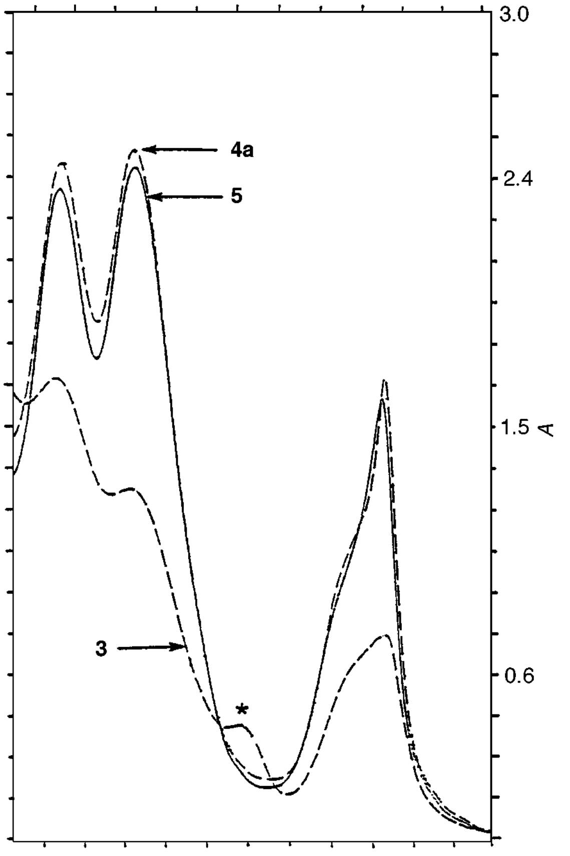


Fig. 2 The UV-VIS spectra of complexes **3**–**5** (* impurity).

reasonable transition state for the polymerization process of **3** to **3***.

Electronic properties of the complexes 3–5

In order to evaluate the influence of the bridge on the electronic properties at the cobalt centre we carried out UV-VIS and cyclic voltammetry studies. The complex $[NEt_4][Co(L^3)_2]$ **5**, with two unbridged ligands, served as a prototype for comparison of bridged and unbridged benzamide 1,2-dithiolate complexes. The UV-VIS spectroscopic data of **3**–**5** are depicted in Fig. 2 and compared in Table 1. The spectra of **3**, **4a** and **5** are very similar indicating the high preference of a square-planar co-ordination geometry. However, while the spectra for **4a** and **5** are almost identical (in spite of the unresolved question of *cis*/*trans* isomerism for **5**), the changed intensity relations and the hypsochromic shift of the bands in the spectra of **3** indicate a slightly different situation at this cobalt(III) centre in accordance with the previously described reactivity pattern.

Table 2 Half-wave potentials of bis(benzenedithiolato)cobaltate complexes: $[Co(L)_2]^- + e^- \rightleftharpoons [Co(L)_2]^{2-}$

Complex	$E_{1/2}$[a]/mV
$[NEt_4][Co(S_2C_6H_4)_2]$[17]	−880[b]
3 $[NEt_4][Co(L^1)]$	−570
4a $[NEt_4][Co(L^2)]$	−510
5 $[NEt_4][Co(L^3)_2]$	−510
$[NEt_4][Co(S_2C_6Cl_4)_2]$[17]	−350[b]

[a] *vs.* Ag–AgCl (3 M KCl solution), solvent dmf. [b] Potential in the original reference *vs.* Ag–AgClO$_4$.

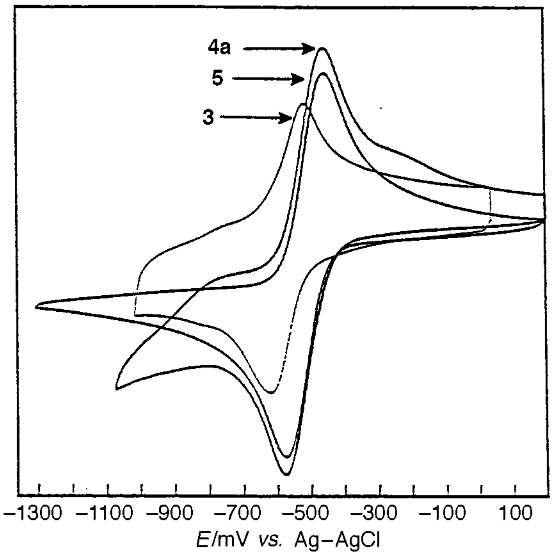


Fig. 3 Cyclic voltammograms of complexes **3**–**5**.

Cyclic voltammetry revealed in a more distinct manner differences between complexes **3** and **4a** (Fig. 3, Table 2). In the range between 0 and −1 V *vs.* Ag–AgCl the redox process $[CoL_2]^-$–$[CoL_2]^{2-}$ could be detected by means of a signal, which shows all the features of a reversible one electron transfer ($\Delta E_p = 65$ mV, $i_{pa}/i_{pc} \approx 1$). The half-wave potential of **5** in dmf was determined to be $E_{1/2} = -510$ mV. This result can be correlated very well with data[17] regarding the electron density in the ligands. The half-wave potential of **5** with benzamide 1,2-dithiolate ligands falls between that of the corresponding complexes with the electron rich $C_6H_4S_2^{2-}$ and the electron deficient $C_6Cl_4S_2^{2-}$ (Table 2).

Complex **4a** with the flexible backbone and the prototype complex **5** exhibit an almost identical half-wave potential ($E_{1/2} = -510$ mV). In contrast, the half-wave potential of **3** with the shorter and more rigid bridge was determined to be $E_{1/2} = -570$ mV. In addition, this electron transfer appears to be less reversible (Figure 3). The reduction of **3**, which is expected to lengthen the metal–sulfur bonds and therefore to add stress to the ligand backbone is more difficult by 60 mV relative to the unbridged and flexibly bridged bis(dithiolate) complexes **4a** and **5**. This result corroborates the assumption that the short and rigid xylylene bridge in $(L^1)^{4-}$ is too small to permit the existence of a thermodynamically stable chelate complex $[Co(L^1)]^-$.

Concluding remarks

We have shown that the electronic properties and the reactivity of the cobalt centre in bis(dithiolato)cobaltate complexes with the new bridged bis(dithiolate) ligands $(L^1)^{4-}$ and $(L^2)^{4-}$ can be manipulated by the character of the bridge, thus by effects originating relatively far from the metal centre in the organic backbone of the ligand. Our experiments indicate that large multidentate ligands with many degrees of freedom do not favor the formation of chelate complexes in a fast reaction like metal halogenide–sodium thiolate metathesis owing to the necessary rearrangement of the ligand during complex formation. In contrast to the fast metathesis reaction, the ligand transfer reactions between the bis(titanocene dithiolate) complexes **1** and **2**, respectively, and tetrachlorocobaltate(II) salts described for the preparation of **3–5** proceed under reflux conditions in the course of hours. The comparatively low reaction rate suggests a high activation enthalpy which turns out to be advantageous for the formation of the chelate complexes **3** and **4a**, **4b**, because the rearrangement barriers for the ligand become negligible under these conditions.

Experimental

If not noted otherwise, all manipulations were performed in an atmosphere of dry argon by using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 spectrometer. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Perkin-Elmer 240 C elemental analyzer. Mass spectra (FAB) were recorded on a Varian MAT CH 5 DF instrument, UV-VIS spectra on a Perkin-Elmer Lambda 9 spectrometer. Cyclic voltammetric data were acquired on Bank High Power Potentiostat Wenking HP 72 and Bank Scan Generator Wenking Model VSG 83 instruments using a platinum working electrode, a Ag–AgCl double junction electrode (3 M KCl solution) as reference and NBu_4ClO_4 as supporting electrolyte; Fc was used as an internal standard and exhibited $E_{1/2} = 480$ mV under these conditions. The complex salts $[NEt_4]_2[CoCl_4]$ and $[NMe_4]_2[CoCl_4]$ were prepared according to ref. 18, $[TiCp_2Cl_2]$ was used as purchased, H_4L^1, $[(TiCp_2)_2(L^1)]$, H_2L^3 and $[TiCp_2(L^3)]$ were prepared as published[9,10] and H_4L^2 was prepared by an identical procedure to that described for H_4L^1[10] using 1,7-diaminoheptane.

Preparations

$[(TiCp_2)_2(L^2)]$ 2. Solid $[TiCp_2Cl_2]$ (293 mg, 1.18 mmol) and subsequently 50 ml thf were added to 0.59 mmol of crude H_4L^2. The addition of 400 µl of triethylamine (2.87 mmol) to the red suspension (undissolved H_4L^2) resulted in a fast change to intense green. After 2 h of stirring the solvent was removed *in vacuo* and the residue redissolved in a little amount of CH_2Cl_2 was put on a chromatographic column (SiO_2). The dinuclear complex **2** was eluted with CH_2Cl_2–CH_3OH (25:1). Thorough drying of the dark green powder *in vacuo* yielded 354 mg of **2** (73%, based on $Pr^i_4L^2$) (Found: C, 60.15; H, 5.13; N, 3.42. $C_{41}H_{42}N_2O_2S_4Ti_2$ requires C, 60.14; H, 5.17; N, 3.42%). NMR: δ_H (250 MHz, $CDCl_3$) 7.61 (d, 2 H, aryl H), 7.48 (d, 2 H, aryl H), 7.22 (t, 2 H, NH), 7.10 (t, 2 H, aryl H), 5.97 (s, br, 20 H, C_5H_5), 3.38 (dt, 4 H, NCH_2), 1.53 (m, 4 H, $NCH_2C\mathit{H}_2$) and 1.32 [m, 6 H, $(CH_2)_3$]; δ_C (62.90 MHz, $CDCl_3$) 168.2 (CO), 158.9, 152.6, 135.4, 131.5, 125.6, 124.4 (aryl C), 113.0 (C_5H_5), 39.8 (NCH_2), 29.3, 28.8 and 26.9 (CH_2).

$[NEt_4][Co(L^1)]$ 3. A solution of 82 mg (0.1 mmol) complex **1** in 70 ml thf was added by syringe to a solution of 46 mg (0.1 mmol) $[NEt_4]_2[CoCl_4]$ in 70 ml CH_3CN. While refluxing this mixture for 12 h it changed slowly from green to blue. After cooling the solvents were removed *in vacuo*. The residue was washed two times with thf (5 ml) in order to remove $[TiCp_2Cl_2]$. Extraction of the crude product **3** with CH_2Cl_2 or dmf and subsequent filtration yielded solutions used for UV-VIS spectroscopy (CH_2Cl_2) and CV (dmf). Keeping the filtered blue solutions in CH_2Cl_2 or CH_3CN resulted in the irreversible precipitation of polymer **3*** in approximate composition concomitant with a decolorisation of the solution. Complex **3**: FAB-MS: *m*/*z* (M^-), 527, $[Co(L^1)]^-$ requires 527. Complex **3***: (Found: C, 54.30; H, 5.64; N, 6.24. $C_{30}H_{36}CoN_3O_2S_4$ requires C, 54.78; H, 5.52; N, 6.39%): UV-VIS λ_{max}/nm (dmf) 321, 366 and 657.

$[NR_4][Co(L^2)]$ (R = Et 4a or Me 4b). A solution of 82 mg (0.1 mmol) complex **2** in 70 ml thf was added by syringe to a solution of 46 mg $[NEt_4]_2[CoCl_4]$ {35 mg $[NMe_4]_2[CoCl_4]$, 0.1 mmol} in 70 ml CH_3CN. While refluxing this mixture for 12 h it changed slowly from green to blue. After cooling the solvents were removed *in vacuo*. The residue was washed two times with thf (5 ml) in order to remove $[TiCp_2Cl_2]$. Diffusion of Et_2O into a solution of crude **4a** in 10 ml CH_3CN resulted at first in the precipitation of by-products. Filtration and cooling the solution to −30 °C yielded 20 mg (30%) **4a** in the form of large thin sheets. FAB-MS: *m*/*z* 521 (M^-), $[Co(L^2)]^-$ requires 521 (Found: C, 53.63; H, 6.52; N, 6.38. $C_{29}H_{42}CoN_3O_2S_4$ requires C, 53.44; H, 6.49; N, 6.45%). In contrast to **4a**, the addition of 10 ml THF to the product mixture **4b** led to a blue solution. Addition of 10 ml toluene, subsequent filtration and cooling to −30 °C resulted in the precipitation of crude **4b**. Thin, needle shaped crystals were obtained by slow cooling of a toluene–acetone (5:1) solution of **4b** from 50 °C to ambient temperature (Found: C, 50.56; H, 5.73; N, 6.99. $C_{25}H_{34}CoN_3O_2S_4$ requires C, 50.40; H, 5.75; N, 7.05%).

$[NEt_4][Co(L^3{}_2]$ 5. A mixture of 190 mg (0.42 mmol) $[TiCp_2(L^3)]$ and 97 mg (0.21 mmol) $[NEt_4]_2[CoCl_4]$ in 30 ml CH_3CN was refluxed for 12 h. Cooling this solution to −30 °C resulted in the precipitation of a blue powder, which was isolated as complex **5**. Diffusion of Et_2O into a CH_3CN solution of **5** yielded 98 mg (63%) of needle shaped blue crystals. FAB-MS: *m*/*z* 605 (M^-), $[Co(L^3)_2]^-$ requires 605; (Found: C, 58.69; H, 5.78; N, 5.71. $C_{36}H_{42}CoN_3O_2S_4$ requires C, 58.76; H, 5.75; N, 5.71%).

Acknowledgements

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References

1 J. D. Franolic, W. Y. Wang and M. Millar, *J. Am. Chem. Soc.*, 1992, **114**, 6587; D. H. Nguyen, H.-F. Hsu, M. Millar, S. A. Koch, C. Achim, E. L. Bominaar and E. Münck, *J. Am. Chem. Soc.*, 1996, **118**, 8963; K. K. Nanda, E. Sinn and A. W. Addison, *Inorg. Chem.*, 1996, **35**, 1; T. Beissel, F. Birkelbach, E. Bill, T. Glaser, F. Kesting, C. Krebs, T. Weyhermüller, K. Wieghardt, C. Butzlaff and A. X. Trautwein, *J. Am. Chem. Soc.*, 1996, **118**, 12376; T. Beissel, T. Glaser, F. Kesting, K. Wieghardt and B. Nuber, *Inorg. Chem.*, 1996, **35**, 3936; P. J. Blower, J. R. Dilworth, J. P. Hutchinson and J. Zubieta, *Transition Met. Chem.*, 1982, **7**, 353.

2 N. de Vries, J. Cook, A. G. Jones and A. Davison, *Inorg. Chem.*, 1991, **30**, 2662; H. Spies, M. Glaser, H.-J. Pietzsch, F. E. Hahn, O. Kintzel and T Lügger, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1418.

3 D. Swenson, N. C. Baenziger and D. Coucouvanis, *J. Am. Chem. Soc.*, 1978, **100**, 1932; N. de Vries, J. C. Dewan, A. G. Jones and A. Davison, *Inorg. Chem.*, 1988, **27**, 1574; T. Maina, A. Pecorale, A. Dolmella, G. Bandoli and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 1994, 2437.

4 D. Sellmann, W. Soglowek, F. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1271; D. Sellmann, W. Soglowek, F. Knoch, G. Ritter and J. Dengler, *Inorg. Chem.*, 1992, **31**, 3711.

5 D. Sellmann, G. H. Rackelmann and F. W. Heinemann, *Chem. Eur. J.*, 1997, **3**, 2071; D. Sellmann, D. Heusinger, F. Knoch and M. Moll, *J. Am. Chem. Soc.*, 1996, **118**, 5368.

6 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49; G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72; R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303; C. Mahadevan, *J. Crystallogr. Spectrosc. Res.*, 1986, **16**, 347.

7 For example: C. Mahadevan, M. Seshasayee, P. Kuppusamy and P. T. Manoharan, *J. Crystallogr. Spectrosc. Res.*, 1985, **15**, 305; D. Sellmann, S. Fünfgelder, F. Knoch and M. Moll, *Z. Naturforsch. Teil B*, 1991, **46**, 1601.

8 G. Henkel, K. Greiwe and B. Krebs, *Angew. Chem.*, *Int. Ed. Engl.*, 1985, **24**, 117.
9 F. E. Hahn and W. W. Seidel, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2700.
10 W. W. Seidel, F. E. Hahn and T. Lügger, *Inorg. Chem.*, 1998, **37**, 6587.
11 C. M. Bolinger and T. B. Rauchfuss, *Inorg. Chem.*, 1982, **21**, 3947; K. Osakada, Y. Kawaguchi and T. Yamamoto, *Organometallics*, 1995, **14**, 4542; T. A. Wark and D. W. Stephan, *Can. J. Chem.*, 1990, **68**, 565.
12 M. Schmidt, B. Block, H. D. Block, H. Köpf and E. Wilhelm, *Angew. Chem.*, *Int. Ed. Engl.*, 1968, **7**, 632; H. W. Roesky, H. Zamankhan, J. W. Bats and H. Fuess, *Angew. Chem.*, *Int. Ed. Engl.*, 1980, **19**, 125.
13 D. T. Sawyer, G. S. Srivatsa, M. E. Bodini, W. P. Schaefer and R. M. Wing, *J. Am. Chem. Soc.*, 1986, **108**, 936.
14 R. Eisenberg, Z. Dori, H. B. Gray and J. A. Ibers, *Inorg. Chem*, 1968, **7**, 741.
15 M. J. Baker-Hawkes, Z. Dori, R. Eisenberg and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 4253.
16 C. G. Pierpont and R. Eisenberg, *Inorg. Chem*, 1970, **9**, 2218; B. Kang, J. Peng, M. Hong, D. Wu, X. Chen, L. Weng, X. Lei and H. Liu, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2897.
17 M. J. Baker-Hawkes, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 4870.
18 J. R. Wiesner, R. C. Srivastva, C. H. L. Kennard, M. DiViara and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **23**, 565.

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