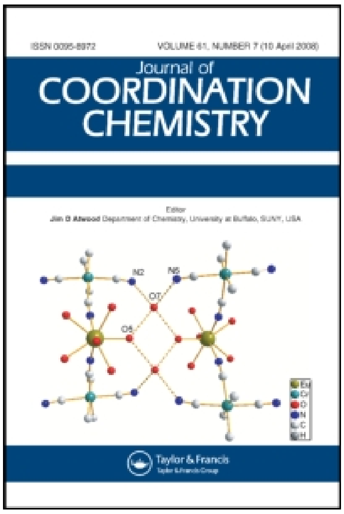

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of tetrahedrally and octahedrally coordinated mixed-valence Co(II)/Co(III) complex with thiosemicarbazone-based ligand

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To cite this Article Panja, Anangamohan and Eichhorn, David M.(2009) 'Synthesis and characterization of tetrahedrally and octahedrally coordinated mixed-valence Co(II)/Co(III) complex with thiosemicarbazone-based ligand', Journal of Coordination Chemistry, 62: 16, 2600 — 2609, First published on: 24 May 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970902915574

URL: http://dx.doi.org/10.1080/00958970902915574

Journal of Coordination Chemistry
Vol. 62, No. 16, 20 August 2009, 2600–2609

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Synthesis and characterization of tetrahedrally and octahedrally coordinated mixed-valence Co(II)/Co(III) complex with thiosemicarbazone-based ligand

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(*Received 2 December 2008; in final form 15 January 2009*)

Synthesis, characterization, and X-ray crystal structure for a mixed-valence binuclear Co(II)/Co(III) complex with the dianionic dithiolate form of a pentadentate ligand 2,6-diacetylpyridinebis(thiosemicarbazone) are reported. A new synthetic methodology has been employed replacing usual cobalt(II) salts by $[Co(NH_3)_5Cl]Cl_2$ as a precursor. The coordination geometry of cobalt(II), CoN_2S_2, was found to be distorted tetrahedral, whereas the cobalt(III) coordination sphere, CoN_4S_2, is slightly distorted octahedral. The magnetic behavior and molar conductivity of the complex are in agreement with the mixed-valence state.

Keywords: Thiosemicarbazone; Mixed-valence Co(II)/Co(III) complex; X-ray crystal structure; Tetrahedral and octahedral coordination sphere

1. Introduction

Interest in the field of thiosemicarbazone chemistry lies in potential biological activity of the ligands and their metal complexes including antitumor [1, 2], fungicidal [3–5], bactericidal [6–8] and antiviral [9] activities. Some pharmaceutical studies have demonstrated that substituents on the 4-N position of thiosemicarbazone or bis(thiosemicarbazone) ligands impart a great influence on their biological activity [10, 11]. Our interest in synthesizing model complexes for the active sites of metalloenzymes with mixed N/S donor sets [12, 13], such as nitrile hydratase [14–18], has led us to investigate the coordination chemistry of this class of ligands.

Coordination of thiosemicarbazone ligands is generally accomplished through the azomethine-N and S atoms. The ligands can bind either through monoanionic thiolate or neutral thiocarbonyl sulfur (scheme 1), and this difference can be monitored crystallographically by measuring the length of the C–S bond. The thiocarbonyl form contains a formal C–S double bond with bond lengths on the order of 1.67–1.72 Å while the thione form undergoes tautomerization to produce a formal C–S single bond with lengths on the order of 1.71 to 1.80 Å [19].

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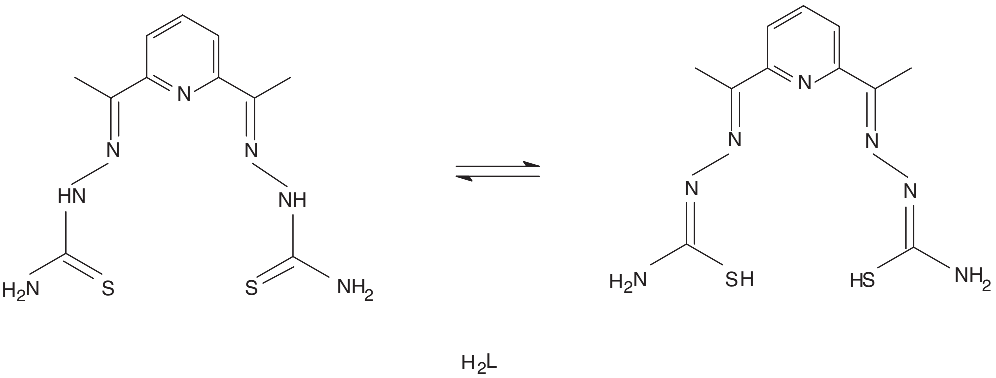
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902915574



Scheme 1. Tautomerization of 2,6-diacetylpyridinebis(thiosemicarbazone).

Although not as intensely studied as monothiosemicarbazones, the bis(thiosemicarbazones) have been the subject of a number of investigations with some indications of biological activity on the part of these ligands and their metal complexes [20]. Structural studies on complexes of thiosemicarbazones with different metals continue to be of interest because these ligands have a variety of coordination modes with π-delocalization of charge and configurational flexibility of their molecular chains [21–30]. Although octahedral cobalt(III) and tetrahedral cobalt(II) complexes are abundant, combination of both in a single molecule is very rare [31]. Coordination chemistry of cobalt has been built using cobalt(II) salts as a starting material but cobalt(III) precursors such as $[Co(NH_3)_5Cl]Cl_2$ have not yet been extensively explored.

We report here the synthesis and crystal structure of a mixed-valence Co(II)/Co(III) complex having two different geometries using $[Co(NH_3)_5Cl]Cl_2$ as precursor, enabling us to compare coordination behavior and biological activities. Spectroscopic, magnetic and other techniques have been employed for structural characterization.

2. Results and discussion

2.1. *Synthesis*

Schiff base condensation of 2,6-diacetylpyridine and thiosemicarbazide produces a N_3S_2 donor set, 2,6-diacetylpyridinebis(thiosemicarbazone) (H_2L). A brownish-red mixed-valence Co(II)/Co(III) complex is achieved on treating the ligand with $[Co(NH_3)_5Cl]Cl_2$. Since $[Co(NH_3)_5Cl]Cl_2$ is kinetically inert, a prolonged reflux is necessary for complete substitution of NH_3.

2.2. *Description of the structure of $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$*

The crystal structure of $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$ is depicted in figure 1 with data collection and structure solution parameters given in table 1. Selected bond distances and angles are shown in table 2. The compound consists of a binuclear cobalt complex cation with helical structure and one disordered chloride counter anion modeled with half-occupancy of each Cl^-. The dimer is situated on a general position in the monoclinic

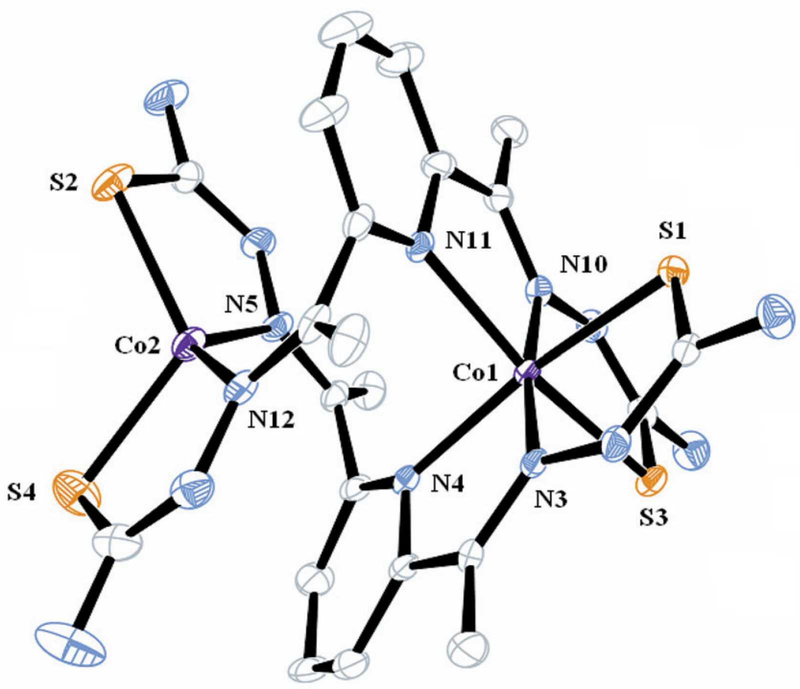


Figure 1. The ORTEP drawing of the cation in $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$ showing 30% ellipsoids. Hydrogen atoms were omitted for clarity.

Table 1. X-ray data collection and structure solution parameters for $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$.

Empirical formula	$C_{22}H_{26}N_{14}S_4ClOCo_2$
Formula weight	784.16
Crystal system	Monoclinic
Space group	Cc (No. 9)
Unit cell dimensions (Å, °)	
a	13.6488(6)
b	23.7853(9)
c	11.0536(4)
α	90
β	105.932(2)
γ	90
V (Å^3)	3450.6(2)
Z	4
D_{Calcd} (g cm^{-3})	1.509
μ (Mo-Kα) (mm^{-1})	1.322
$F(000)$	1596
T (K)	150(2)
γ (Mo-Kα)	0.71073
Maximum and minimum θ range (°)	27.20–1.71
Total data, unique data	44,639, 7159
Observed data [$I > 2\sigma(I)$]	6332
R_{int}	0.0426
R_1, wR_2 [$I > 2\sigma(I)$]	0.0503, 0.1542
R_1, wR_2 (all)	0.0608, 0.1651
Goodness-of-fit	1.088

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Co^{II}Co^{III}L_2}]\mathrm{Cl}\cdot\mathrm{H_2O}$.

Co1–S1	2.2236(14)	Co1–S3	2.2287(14)
Co1–N3	1.898(5)	Co1–N4	2.025(5)
Co1–N10	1.889(5)	Co1–N11	2.019(5)
Co2–S2	2.2676(18)	Co2–S4	2.2409(19)
Co2–N5	2.045(5)	Co2–N12	2.034(5)
S1–C1	1.748(6)	S2–C11	1.748(7)
S3–C12	1.757(6)	S4–C22	1.736(7)
S1–Co1–S3	91.81(6)	S1–Co1–N3	85.64(14)
S1–Co1–N4	167.59(15)	S1–Co1–N10	90.17(14)
S1–Co1–N11	85.81(13)	S3–Co1–N3	89.49(14)
S3–Co1–N4	86.64(13)	S3–Co1–N10	85.67(15)
S3–Co1–N11	166.79(15)	N3–Co1–N4	82.04(19)
N3–Co1–N10	173.5(2)	N3–Co1–N11	103.3(2)
N4–Co1–N10	101.98(19)	N4–Co1–N11	98.41(18)
N10–Co1–N11	81.3(2)	S2–Co2–S4	120.53(8)
S2–Co2–N5	85.43(14)	S2–Co2–N12	122.39(14)
S4–Co2–N5	114.80(14)	S4–Co2–N12	85.62(15)
N5–Co2–N12	132.08(19)		

space group *Cc* and crystallizes with 1 molecule of water per dimer. Each ligand is dianionic using SNNNS donors *via* the pyridine nitrogen, two azomethine nitrogens, and the two thiolate sulfurs. Each ligand bridges two cobalts, with the pyridine and one arm of each ligand occupying three meridional sites on the octahedral Co(1), and the thiolate and azomethine donors of the other arm of each ligand on the tetrahedral Co(2). In order to achieve this geometry, a rotation of 60° around the C–C bond between the pyridine ring and the imine carbon is necessary (torsion angles for N4–C8–C9–N5 and N11–C19–C20–N12 are 56.4 and 60.8°, respectively), resulting in a double helical structure (figure 2). This coordination requires that the cobalt centers have different coordination and geometry, six for the slightly distorted octahedral N_4S_2 environment for Co(1) and distorted tetrahedral for the four coordinated Co(2). The planes defined by the five-membered rings Co2–N5–N6–C11–S2 and Co2–N12–N13–C22–S4 deviate from perpendicular (dihedral angle 83.9°) indicating the distortion at Co(2). The most deviated chelate bite angles S2–Co2–N5 and N5–Co2–N12 are 85.43 and 132.08°, respectively, for the distorted tetrahedral geometry. In a binuclear Co(II)/Co(II) complex with the same ligand, reported earlier, the ligand is also bonded with all five donors, the major difference being that it is a neutral ligand, ligated through the thiocarbonyl-S and both cobalts are pentagonal bipyramidal [13]. Therefore, the thiolate and thiocarbonyl tautomeric forms have an impact on the structural pattern. Changing of the precursor to $[Co(NH_3)_5Cl]Cl_2$ instead of the usual cobalt(II) salt may also have some influence. The present structure can be correlated with reported binuclear zinc complexes with similar thiosemicarbazone ligands [23, 29]; helicity of such ligands is achievable if ligands are bonded through dianionic dithiolates. In most cases with metal centers in +2 oxidation states, neutral dihelicates are the products. Cationic helicate complexes have generally been found for neutral N-donor ligand systems ([29] and references therein). However, in the present case we have isolated a very uncommon helical cationic complex with the pentadentate dianionic dithiolate form of the thiosemicarbazone ligand.

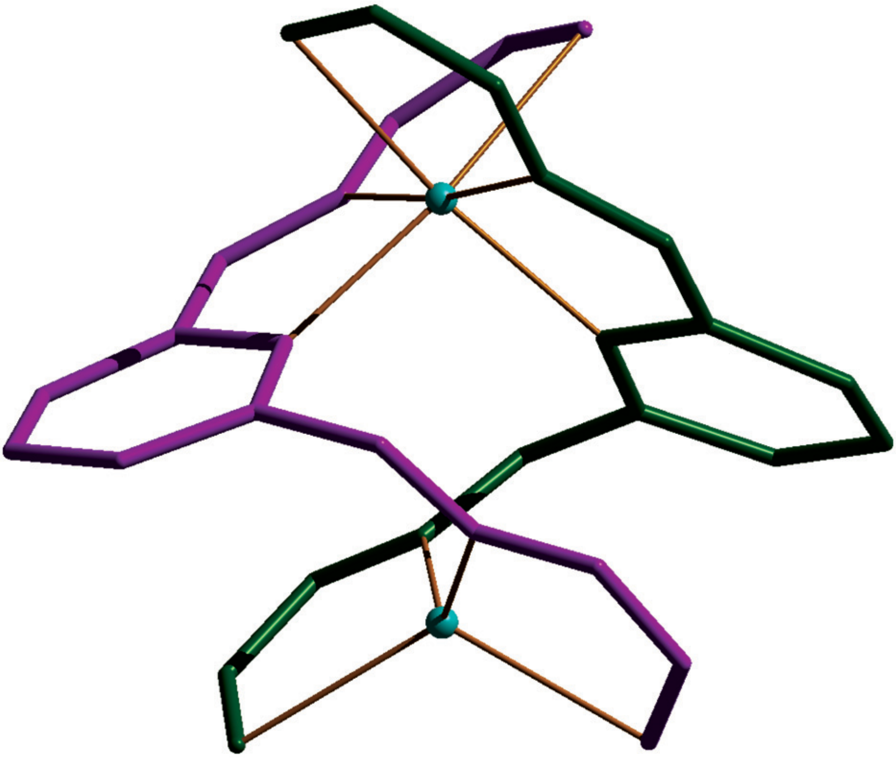


Figure 2. Ball-and-stick representation of dihelicate structure of $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$ with the two strands of L highlighted in pink and green.

Assignment of oxidation states of cobalt can be made by comparing the bond distances at the two cobalt centers. The average bond distances of Co(III)–N(azomethine), Co–N(py), and Co–S are 1.903, 2.018, and 2.226 Å, respectively, coordinated to the Co(1) center, in agreement with the corresponding bond distances in literature for octahedral cobalt(III) [13, 32, 33]. The Co–N(azomethine) bond distances are shorter than Co–N(py) bond distances, indicating greater bond strength [5, 34]. The average bond distances of Co–N(azomethine) and Co–S at the Co(II) are 2.045 and 2.240 Å, respectively. Bond distances of Co–S at both cobalt centers cannot differentiate the oxidation states because in a large number of cases bond distances of Co–S(thiolate) fall in the same range for both octahedral low spin Co(III) and high spin tetrahedral Co(II) [35–38]. However, deviation of the Co–N(azomethine) bond distances of about 0.14 Å, typical for differences between corresponding bonds of high spin Co(II) and low spin Co(III) centers, clearly suggests the oxidation state of Co(2) is +2, and the bond distances of Co–N(azomethine) are comparable with the reported values where imine nitrogen is bonded to a cobalt(II) center in a tetrahedral environment [39–41]. The intramolecular separation of these two cobalt centers is 3.92 Å. Crystallographic characterization unexpectedly identified the mixed-valence dinuclear Co(II)/Co(III) complex, although the reductant has not been identified. A few iron(II) complexes have also been prepared by reaction of similar pentadentate thiosemicarbazone

Table 3. Electrochemical[a] and electronic spectral[b] data for $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$.

λ_{max} (nm) [ε ($dm^3 mol^{-1} cm^{-1}$)]	$E_{1/2}$ (V)	ΔE_p (V)	E_{irr} (V)
1250 (160), 650 (275), 695 (sh), 360 (11,500), 245 (29,400)	−1.0	0.20	0.85

[a] Solvent: acetonitrile; working electrode: platinum; reference electrode: SCE; E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $E_{1/2} = 0.5(E_{pa} + E_{pc})$; $\Delta E_p = E_{pa} - E_{pc}$; scan rate: $50 mV s^{-1}$.
[b] Molar absorption coefficient is given per dimer in acetonitrile.

ligands using iron(III) precursors [13, 28]. The affirmation of mixed-valence state is further supported by other physiochemical properties described in the following sections. Molecular packing is stabilized by strong hydrogen bonds involving terminal NH_2 of the ligand, Cl^- and water of crystallization.

2.3. *IR and electronic spectroscopy*

The most significant IR bands are listed in the experimental section. A relatively broad band at $3426 cm^{-1}$ is due to a combination of the stretching frequencies of N–H and O–H of amine and water of crystallization. Bands from 1356 to $1617 cm^{-1}$ attributed to ν(C=C) and ν(C=N) experience significant shifts in the spectra of the complex, and their mixing patterns are different from that in the spectrum of the ligand. The positive shift of ν(C=N) in the range $1597 cm^{-1}$ in the free ligand to $1617 cm^{-1}$ in the complex is consistent with coordination of the azomethine nitrogen to cobalt [42]. Bands at 1095 and $890 cm^{-1}$, due to ν(C=S) and δ(C=S), respectively, of the free ligands, are shifted to lower wavenumbers, indicating coordination of thiolate sulfur to cobalt. The downward shift of the bands in the complex can be attributed to a change of bond order and strong delocalization of electrons upon coordination.

Data from the electronic spectrum of the mixed-valence complex are shown in table 3. The spectrum consists of an absorption in the NIR region of low intensity (1250 nm) and a relatively stronger broad band in the visible region at 650 nm. Both bands are consistent with Co(II) with tetrahedral geometry [31, 43]. There are also peaks at 360 and 245 nm which can be assigned as L → M and L → L charge transfer, respectively.

2.4. *Electrochemistry*

To investigate the electron transfer of $[Co^{II}Co^{III}L_2]Cl \cdot H_2O$, cyclic voltammetry was performed in acetonitrile solution within the potential range +1.5 to −1.5 V *versus* the saturated calomel electrode (SCE) at ambient temperature using TEAP as supporting electrolyte. The voltammogram of the complex is in figure 3 and the electrochemical data are shown in table 3. The complex displayed a quasireversible reductive response at −1.0 V with characteristic cathodic (E_{pc}) and anodic (E_{pa}) peak potentials at −1.1 and −0.90 V, respectively. The quasireversible signal is attributed to the reduction of Co(III) to Co(II), and the relevant electron transfer is shown in Equation (1). In addition, an irreversible oxidation peak is observed at $E_{irr} = 0.85$ V. The electrochemical irreversibility possibly arises from the instability of the Co(III) center in the tetrahedral environment.

$$\mathrm{Co(III)Co(III)} \xleftarrow{-e} \mathrm{Co(II)Co(III)} \xrightleftharpoons{+e} \mathrm{Co(II)Co(II)} \qquad (1)$$

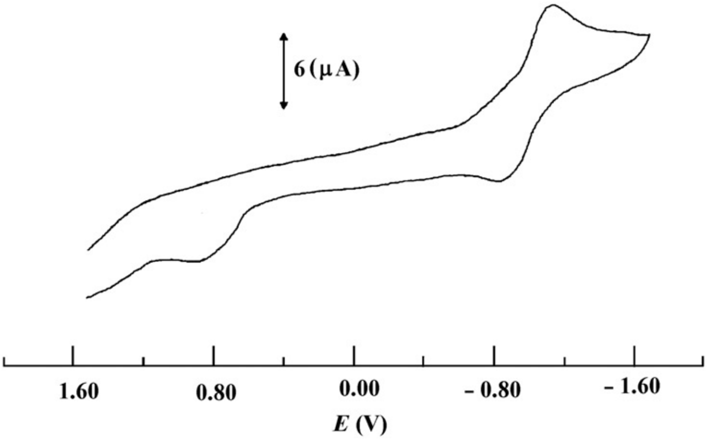


Figure 3. Cyclic voltammogram (scan rate 50 mV s^{-1}) of [Co^{II}Co^{III}L$_2$]Cl · H$_2$O in acetonitrile at a platinum electrode with the internal standard ferrocene and TEAP as supporting electrolyte.

2.5. *Magnetochemistry and conductivity*

The room temperature magnetic moment value per dimer ($\mu_{eff} = 4.56$ BM) is within the range observed for mononuclear tetrahedral cobalt(II) complexes. The effective magnetic moment is larger than the spin-only value of 3.87 BM for high spin cobalt(II), reflecting a significant degree of orbital contribution. This behavior is typical for cobalt(II) complexes irrespective of their coordination environment [44, 45].

The molar conductivity value of 105 Ω^{-1} cm^2 mol^{-1} in DMF solution reflects the existence of a 1 : 1 electrolyte in the solution, definitely supporting the mixed-valence state of cobalt in [Co^{II}Co^{III}L$_2$]Cl · H$_2$O [46].

3. Conclusion

A new mixed-valence Co(II)/Co(III) complex has been synthesized and characterized employing [Co(NH$_3$)$_5$Cl]Cl$_2$ as a precursor complex. Each of the N$_3$S$_2$ donor thiosemicarbazone ligands coordinates to the metal centers in a helicate. Although it is not relevant as a nitrile hydratase model complex, other biological activity of this compound will be pursued.

4. Experimental

4.1. *Materials*

All chemicals and solvents used for the synthesis were of reagent grade, purchased from commercial sources and used without purification. Solvents were purified and dried using standard methods. The [Co(NH$_3$)$_5$Cl]Cl$_2$ [47] and pentadentate N$_3$S$_2$ donor Schiff-base ligand (H$_2$L) were synthesized following the procedure given in [20].

4.2. *Physical measurements*

Microanalysis (CHN) was performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrophotometer with samples prepared as KBr pellets. UV-Vis-NIR spectroscopic measurements were carried out on a JASCO V-750 spectrophotometer equipped with thermostated cell compartments. Conductivity measurements were made with a Systronics (India) direct reading conductivity meter (model 304) and magnetic susceptibility measurements were carried out on a PAR 155 vibrating sample magnetometer. The data were corrected for diamagnetic susceptibilities using Pascal's constants. Cyclic voltammetry was performed at a platinum electrode using an EG&G PARC electrochemical analysis system (Model 250/5/0) in acetonitrile under dry nitrogen atmosphere in conventional three electrode configurations with a scan rate of $0.05\,\mathrm{V\,s^{-1}}$.

4.3. *Synthesis of $[Co^{II}Co^{III}L_2]Cl\cdot H_2O$*

To 50 mL of ethanol, 310 mg (2 mmol) of 2,6-diacetylpyridinebis(thiosemicarbazone) and 500 mg (1 mmol) of $[Co(NH_3)_5Cl]Cl_2$ was added. The mixture was refluxed for 2 days, giving a brownish-red solution. The resulting mixture was evaporated to dryness and extracted with methanol, volume was reduced to 10 mL and, upon standing at room temperature, 240 mg (0.3 mmol, 60%) of $[Co^{II}Co^{III}L_2]Cl\cdot H_2O$ was isolated as a brownish-red crystalline material. X-ray quality crystals were grown by slow evaporation of a solution in ethanol–methanol. Anal. Calcd for $C_{22}H_{28}N_{14}S_4ClOCo_2$ (%): C, 33.58; H, 3.56; N, 24.93. Found: C, 33.83; H, 3.46; N, 24.45. IR (KBr pellet, cm^{-1}): 3426br, 1617vs, 1581s, 1384m, 1356m, 1194m, 1113w, 1020w, 827w, 783w, 755w, 673w, 594w (br, broad; vs, very strong; s, strong; m, medium; w, weak).

4.4. *X-ray crystallography*

Single crystals of $[Co^{II}Co^{III}L_2]Cl\cdot H_2O$ were grown by slow evaporation of a methanol–ethanol solution of the complex. Data for $[Co^{II}Co^{III}L_2]Cl\cdot H_2O$ were collected using a Bruker Kappa APEXII diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.71073\,\text{Å}$] equipped with an Oxford Cryosystems Cryostream 700 low-temperature apparatus. A suitable crystal of dimensions $0.52 \times 0.32 \times 0.15\,\mathrm{mm^3}$ was identified under a polarizing microscope and affixed with oil in a Hampton Research Cryoloop and transferred to the cold stream of the diffractometer. Data reduction was performed using Bruker SAINT [48] software, structure solution (direct methods) and refinement (full-matrix least-squares) using SHELXS-97 and SHELXL-97 [49] within the Bruker SHELXTL suite. Data were corrected for Lorentz and polarization effects and for absorption using the Bruker SADABS [48] program (multiscan). Hydrogen atoms were placed at calculated idealized positions and were not refined. All non-hydrogen atoms were refined using anisotropic thermal parameters. Pertinent details are given in table 1.

Supplementary material

Crystallographic data for the structural analysis has been deposited to Cambridge Crystallographic Data Centre; CCDC reference number for

$[Co^{II}Co^{III}L_2]Cl \cdot H_2O$ is 708956. Copy of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44-(1223)-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgements

This work was supported by NIH COBRE Award P20 RR017708 from the National Center for Research Resources (D.M.E.). A.P. would like to thank Professor Pradyot Banerjee, Indian Association for the Cultivation of Science, for providing laboratory facilities and helpful discussions.

References

[1] E.J. Blanz, F.A. French. *Cancer Res.*, **28**, 2419 (1968).
[2] D. Kovala-Demertzi, M.A. Demertzis, J.R. Miller, C. Papadopoulou, C. Dodorou, G. Filousis. *J. Inorg. Biochem.*, **86**, 555 (2001).
[3] S.P. Mittal, S.K. Sharma, R.V. Singh, J.P. Tandon. *Curr. Sci.*, **50**, 483 (1981).
[4] E. Bermejo, R. Carballo, A. Castiñeiras, R. Dominguez, A.E. Liberta, C. Maichle-Mössmer, M.M. Salberg, D.X. West. *Eur. J. Inorg. Chem.*, 965 (1999).
[5] M.C. Rodríguez-Argüelles, E.C. López-Silva, J. Sanmartín, A. Bacchi, C. Pelizzi, F. Zani. *Inorg. Chim. Acta*, **357**, 2543 (2004).
[6] A.S. Dobeck, D.L. Klayman, E.J. Dickson, J.P. Scovill, E.C. Tramont. *Antimicrob. Agents Chemother.*, **18**, 27 (1980).
[7] N.C. Kasuga, K. Sekino, C. Koumo, N. Shimada, M. Ishikawa, K. Nomiya. *J. Inorg. Biochem.*, **84**, 55 (2001).
[8] K. Nomiya, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, N.C. Kasuga, H. Yokoyama, S. Nakano, K. Onodera. *J. Inorg. Biochem.*, **98**, 601 (2004).
[9] J.C. Logan, M.P. Fox, J.H. Morgan, C.J. Pfau. *J. Gen. Virol.*, **28**, 271 (1975).
[10] G.M. Abu El-Reasch, M.A. Khattab, U.I. El-Ayaan. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1417 (1992).
[11] P.W. Sadler. *Ann. NY Acad. Sci.*, **130**, 71 (1965).
[12] B.W. Smucker, M.J. Van Stipdonk, D.M. Eichhorn. *J. Inorg. Biochem.*, **101**, 1537 (2007).
[13] A. Panja, C. Campana, C. Leavitt, M.J. Van Stipdonk, D.M. Eichhorn. *Inorg. Chim. Acta*, **362**, 1348 (2009).
[14] A. Miyanaga, S. Fushinobu, K. Ito, T. Wakagi. *Biochem. Biophys. Res. Commun.*, **288**, 1169 (2001).
[15] B.A. Brennan, G. Alma, M.J. Nelson, L.T. Durney, R.C. Scarrow. *J. Am. Chem. Soc.*, **118**, 9194 (1996).
[16] M.S. Payne, S. Wu, R.D. Fallon, G. Tudor, B. Stieglitz, I.M. Turner, M.J. Nelson. *Biochemistry*, **36**, 5447 (1997).
[17] M. Odaka, K. Fujii, M. Hoshino, T. Noguchi, M. Tsujimura, S. Nagashima, M. Yohda, T. Nagamune, Y. Inoue, I. Endo. *J. Am. Chem. Soc.*, **119**, 3785 (1997).
[18] T. Nagasawa, K. Takeuchi, H. Yamada. *Eur. J. Biochem.*, **196**, 581 (1991).
[19] Range established by a search of the Cambridge Structural Database: F.H. Allen. *Acta Crystallogr.*, *Sect. B*, **58**, 380 (2002).
[20] M. Mohan, P. Sharma, M. Kumar, N.K. Jha. *Inorg. Chim. Acta*, **125**, 9 (1986).
[21] A.I. Matesanz, I. Cuadrado, C. Pastor, P. Souza. *Z. Anorg. Allg. Chem.*, **631**, 780 (2005).
[22] G.F. de Sousa, D.X. West, C.A. Brown, J.K. Swearingen, J. Valdes-Martinez, R.A. Toscano, S. Hernandez-Ortega, M. Homer, A.J. Bortoluzzi. *Polyhedron*, **19**, 841 (2000).
[23] M.R. Bermejo, A.M. González-Noya, R.M. Pedrido, M.J. Romero, M. Vázquez. *Angew. Chem., Int. Ed. Engl.*, **44**, 4182 (2005).
[24] E. Labisbal, A. Castiñeiras, C.A. Brown, D.X. West. *Z. Naturforsch.*, **B 56**, 229 (2001).
[25] M.S. Shongwe, H.N.R. Al-Kharousi, H. Adams, M.J. Morris, E. Bill. *Inorg. Chem.*, **45**, 1103 (2006).
[26] A. Bino, N. Cohen. *Inorg. Chim. Acta*, **210**, 11 (1993).
[27] A.H. Othman, K.-L. Lee, H.-K. Fun, B.-C. Yip. *Acta Crystallogr., Sect. C*, **52**, 602 (1996).
[28] G. Dessy, V. Fares. *Cryst. Struct. Commun.*, **10**, 1025 (1981).

[29] R. Pedrido, M.R. Bermejo, M.J. Romero, M. Vázquez, A.M. González-Noya, M. Maneiro, M.J. Rodríguez, M.I. Fernández. *Dalton Trans.*, 572 (2005).
[30] C.A. Brown, W. Kaminsky, K.A. Claborn, K.I. Goldberg, D.X. West. *J. Braz. Chem. Soc.*, **13**, 10 (2002).
[31] B. Chiari, A. Cinti, O. Crispu, F. Demartin, A. Pasini, O. Piovesana. *J. Chem. Soc., Dalton Trans.*, 3611 (2001).
[32] H.-S. Wang, L. Huang, Z.F. Chen, X.-W. Wang, J. Zhou, S.-M. Shi, H. Liang, K.-B. Yu. *Acta Cryst.*, **E60**, m354 (2004).
[33] J. García-Tojal, G. García-Orad, A.A. Díaz, J.L. Serra, M.K. Urtiaga, M.I. Arriortua, T. Rojo. *J. Inorg. Biochem.*, **84**, 271 (2001).
[34] C.-Y. Duan, Z.-H. Liu, X.-Z. You, F. Xue, T.C.W. Mak. *Chem. Commun.*, 381 (1997).
[35] Y.-X. Tong, C.-Y. Su, B.-S. Kang, X.-L. Yu, X.-M. Chen. *Acta Cryst., Sect. C*, **C55**, 1800 (1999).
[36] N. Duran, W. Clegg, L. Cucurull-Sánchez, R.A. Coxall, H.R. Jiménez, J.-M. Moratal, F. Lloret, P. González-Duarte. *Inorg. Chem.*, **39**, 4821 (2000).
[37] C. Bru1ckner, S.J. Rettig, D. Dolphin. *Inorg. Chem.*, **39**, 6100 (2000).
[38] H.K. Lee, C.H. Lam, S.-L. Li, Z.-Y. Zhang, T.C.W. Mak. *Inorg. Chem.*, **40**, 4691 (2001).
[39] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Laschi. *Organometallics*, **22**, 2545 (2003).
[40] S.A. Carabineiro, L.C. Silva, P.T. Gomes, L.C.J. Pereira, L. Veiros, S.I. Pascu, M.T. Duarte, S. Namorado, R.T. Henriques. *Inorg. Chem.*, **46**, 6880 (2007).
[41] D.T. Corwin Jr, R. Fikar, S.A. Koch. *Inorg. Chem.*, **26**, 3079 (1887).
[42] P.F. Rapheal, E. Manoj, M.R. Prathapachandra Kurup, E. Suresh. *Polyhedron*, **26**, 607 (2007).
[43] D. Swenson, N.C. Baenziger, D. Coucouvanis. *J. Am. Chem. Soc.*, **100**, 1932 (1978).
[44] D.A. Safina, P. Mlynarz, F.E. Hahn, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski. *Z. Anorg. Allg. Chem.*, **633**, 1472 (2007).
[45] M.C. Aragoni, M. Arca, M.B. Carrea, A. Garau, F.A. Devillanova, F. Isaia, V. Lippolis, G.L. Abbati, F. Demartin, C. Silvestru, S. Demeshko, F. Meyer. *Eur. J. Inorg. Chem.*, 4607 (2007).
[46] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[47] S.M. Jörgensen. *Z. Anorg. Chem.*, **17**, 461 (1898).
[48] *APEX2 User Manual*, Bruker AXS, Inc., Madison, WI (2006).
[49] G.M. Sheldrick. Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany (1998).