Synthesis, Spectra and Crystal Structure of Two Copper(I) Complexes of Acetonethiosemicarbazone

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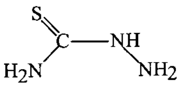
The reaction of copper(I) chloride with acetonethiosemicarbazone (tscac) in a copper to tscac molar ratio of 1:2 forms the cationic complex [Cu(tscac)$_2$]Cl (**1**). When the ratio of the copper to tscac was reduced to 1:1, a dimeric complex [Cu$_2$Cl$_2$(tscac)$_2$]$_2$ (**2**) was obtained. In complex **2**, two CuCl$_2$ species act as bridging groups between two Cu(tscac)$_2$ moieties forming an eight-membered ring, whereas in complex **1**, there is no CuCl$_2$ moiety in the structure. In both complexes the copper(I) center is coordinated in a distorted tetrahedral geometry to two tscac groups through the sulfur and the imine nitrogen atom. In dimeric complex **2**, the sulfur atom in each tscac ligand coordinates weakly to copper(I) in the CuCl$_2$ moiety giving the distorted tetrahedral geometry. For the free ligand, the $\nu_{C=S}$ vibration at 789 cm^{-1} appears at lower energy than in complexes **1** and **2** (754 and 744 cm^{-1} respectively) indicating coordination at the sulfur atom. The complexes synthesized by either electrochemical or chemical methods are identical.

Introduction

Thiosemicarbazone and its derivatives are chelating ligands with sulfur and nitrogen donor atoms forming a five-membered chelate ring. In a few cases they behave as monodentate ligands and bond through the sulfur atom only.[1] These ligands show antitubercular activity and activity against influenza and have been suggested as possible pesticides and fungicides. These activities are due to their ability to chelate trace metals. It has been reported that copper ions enhance the antitubercular activity of thiosemicarbazone,[2] leading to an increased interest in the chemistry of transition metal chelates of thiosemicarbazone and its derivatives. The preparation and crystal structures of copper(II) complexes of thiosemicarbazide, thiosemicarbazone and their derivatives have been reported.[3−8] The copper(I) complexes of some *N*- and *S*-substituted thiosemicarbazones are polymeric, the metal ion being bonded through the nitrogen and sulfur of the thiosemicarbazone moiety.[1] We report here a comparison of the crystal structures of two copper(I) complexes of acetonethiosemicarbazone, i.e. [Cu(tscac)$_2$]Cl (**1**) and [Cu$_2$Cl$_2$(tscac)$_2$]$_2$ (**2**) which were prepared by both chemical and electrochemical methods. Their spectroscopic data are also reported.



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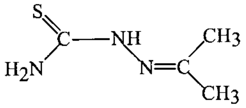

(tscac)

Results and Discussion

Electrolysis of elemental copper in an ammonium chloride solution containing the ligand for half an hour at 4.5 V and 40 mA was found to be optimum for the formation of complex **1** with the highest yield (98%). A total of 72 coulombs of electricity was passed leading to the dissolution of 0.054 g of copper. The electrochemical efficiency (E_f), which is defined as mol of metal dissolved per Faraday of electricity, was found to be 1.14. This means the anodic reaction involves a one-electron transfer. For the preparation of complex **2**, the optimum conditions for the electrolysis were one hour at 3.5 V and 40 mA. The 144 coulombs of electricity applied led to the dissolution of 0.108 g of copper. The electrochemical efficiency (E_f) was found to be 0.96. This means the anodic reaction also involves a one-electron transfer.[9] X-ray analyses for these complexes showed that the complexes prepared by both chemical and electrochemical methods have the same molecular and crystal structures. Consequently, only the crystal structures of com-

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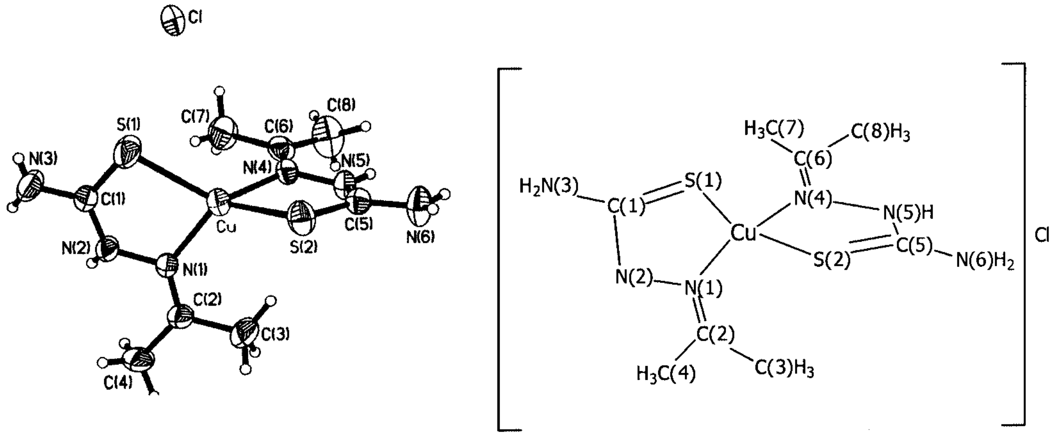


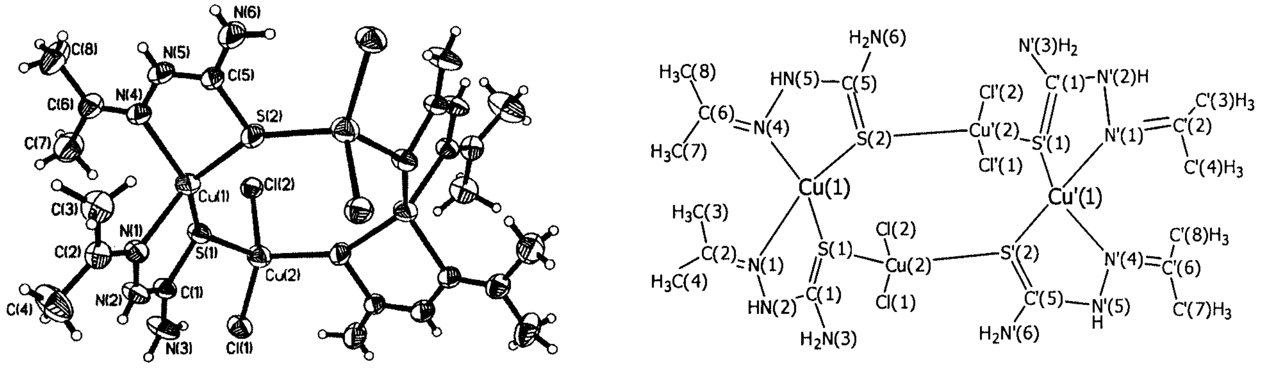
(a) (b)

Figure 1. (a) Perspective view of complex **1** with thermal ellipsoids at the 50% probability level; (b) structural formula

plexes **1** and **2** prepared by chemical methods are discussed below.

Complex **1** consists of a distorted tetrahedral $[Cu(tscac)_2]^+$ cation and a chloride counteranion (Figure 1). The copper tetrahedron consists of two sulfurs and two nitrogens of two acetonethiosemicarbazone ligands forming two five-membered chelate rings. All the atoms of the five-membered rings are essentially coplanar and the planes of those rings are almost perpendicular. The average Cu−S distance is similar to the Cu−S distance in $[Cu(tsc)Cl_2]$.[3]

Complex **2** crystallizes as a neutral tetranuclear copper(I) complex with general formula $[Cu_2Cl_2(tscac)_2]_2$. Two $Cu(tscac)_2$ moieties are bridged by two $CuCl_2$ groups forming an eight-membered ring. In each $Cu(tscac)_2$ moiety, a copper center [Cu(1)] is coordinated in a distorted tetrahedral geometry by two sulfur atoms [S(1) and S(2)] and two nitrogen atoms [N(1) and N(4)] of two tscac ligands, forming two five-membered rings as in complex **1**. The coordination around the other copper center [Cu(2)] in the bridging $CuCl_2$ is also tetrahedral. Each $CuCl_2$ acts as a bridging group between two $Cu(tscac)_2$ moieties through the S(1) and S(2) atoms and gives rise to the tetranuclear copper(II) complex shown in Figure 2. The imino protons of the two tscac ligands are non-equivalent and give rise to NMR signals at $\delta = 10.31$ and 11.41 ppm. The center of each molecule is a crystallographic center of symmetry which is surrounded by four copper and four sulfur atoms forming an eight-membered ring. The two Cu−Cl distances are significantly different by 0.08 Å and longer than those for $[Cu^{II}(tsc)Cl_2]$.[3] The elongation of the Cu−Cl bond in this complex may be a result of the spatial arrangement of a hydrogen bonding interaction between the amino group and the chloride ion. The closest hydrogen bond length is 3.159 Å between N(3) and Cl(1). This interaction causes the non-equivalence of the amino protons. The torsion angles Cl(1)−Cu(2)−S(1)−C(1), Cl(2)−Cu(2)−S(1)−C(1) and Cu(2)−S(1)−C(1)−N(3) are 22.19(15)°, 140.89(14)° and −22.3(4)°, respectively, showing that the Cl(1) and N(3) atoms are in a suitable position for the formation of an intramolecular hydrogen bond. The Cu(1)−S bond length is 0.01 Å shorter than the Cu(2)−S bond length, indicating the weaker nature of the Cu(2)−S bond. As Cu(1) is part of two five-membered rings the length of the Cu(1)−S bond must be squeezed. The molecule forms weak intermolecular hydrogen bonds as indicated in Figure 3. The formation of two five-membered rings around Cu(1) causes the deviation of the angles around Cu(1) from tetrahedral angles, and this deviation is greater than that around Cu(2). The angle between the planes of the two five-membered rings is almost perpendicular (approx. 80°). All the atoms of the five-



(a) (b)

Figure 2. (a) Perspective view of complex **2** with thermal ellipsoids at the 50% probability level; (b) structural formula

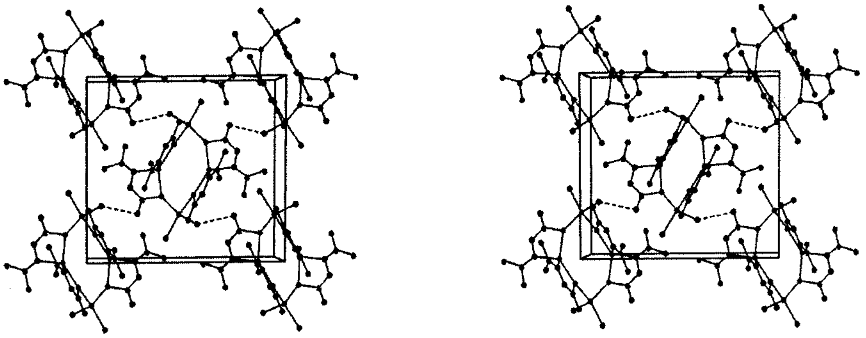


Figure 3. A stereoscopic view of the packing in the unit cell of $[Cu_2Cl_2(tscac)_2]_2$ (**2**) showing the intermolecular hydrogen bonding

Table 1. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

	Compound **1**		
Cu−N(1)	2.1031(14)	Cu−N (4)	2.1657(14)
Cu−S(1)	2.2598(5)	Cu−S(2)	2.2737(6)
S(1)−C(1)	1.6900(19)	S(2)−C(5)	1.6988(17)
N(1)−C(2)	1.289(2)	N(1)−N(2)	1.3921(19)
N(2)−C(1)	1.350(2)	N(3)−C(1)	1.327(2)
N(4)−C(6)	1.285(2)	N(4)−N(5)	1.3930(19)
N(5)−C(5)	1.349(2)	N(6)−C(5)	1.328(2)
C(2)−C(3)	1.493(3)	C(2)−C(4)	1.494(3)
C(6)−C(8)	1.493(3)	C(6)−C(7)	1.494(3)
N(1)−Cu−N(4)	107.80(5)	N(1)−Cu−S(2)	127.69(4)
N(4)−Cu−S(2)	85.10(4)	N(1)−Cu−S(1)	86.30(4)
N(4)−Cu−S(1)	124.05(4)	S(2)−Cu−S(1)	128.51(2)
	Compound **2**		
Cu(1)−N(4)	2.084(3)	Cu(1)−N(1)	2.117(3)
Cu(1)−S(1)	2.2647(11)	Cu(1)−S(2)	2.2762(11)
Cu(2)−Cl(1)	2.3157(11)	Cu(2)−S(2)*	2.3405(12)
Cu(2)−S(1)	2.3678(11)	Cu(2)−Cl(2)	2.3936(12)
S(1)−C(1)	1.708(4)	S(2)−C(5)	1.713(4)
S(2)−Cu(2)*	2.3405(12)	N(1)−C(2)	1.290(5)
N(1)−N(2)	1.396(4)	N(2)−C(1)	1.340(5)
N(3)−C(1)	1.325(5)	N(4)−C(6)	1.280(5)
N(4)−N(5)	1.402(5)	N(5)−C(5)	1.336(5)
N(6)−C(5)	1.317(5)	C(2)−C(3)	1.482(6)
C(2)−C(4)	1.503(7)	C(6)−C(8)	1.495(7)
C(6)−C(7)	1.505(7)		
N(4)−Cu(1)−N(1)	105.49(12)	N(4)−Cu(1)−S(1)	126.81(10)
N(1)−Cu(1)−S(1)	86.10(8)	N(4)−Cu(1)−S(2)	85.99(9)
N(1)−Cu(1)−S(2)	125.08(9)	S(1)−Cu(1)−S(2)	129.33(5)
Cl(1)−Cu(2)−S(2)*	114.85(4)	Cl(1)−Cu(2)−S(1)	114.37(4)
S(2)*−Cu(2)−S(1)	106.76(4)	Cl(1)−Cu(2)−Cl(2)	111.21(4)
S(2)*−Cu(2)−Cl(2)	108.78(5)	S(1)−Cu(2)−Cl(2)	99.68(4)

membered rings are essentially coplanar. The principle distances and angles are presented in Table 1.

A comparison between the vibrational bands of tscac in $[Cu(tscac)_2]Cl$ and $[Cu_2Cl_2(tscac)_2]_2$ leads to the following observations:

(1) The absorption bands at 2800−3300 cm^{-1} are assigned to NH_2 and N−H stretching modes.[8] A broad peak at 3554 cm^{-1} in the spectrum of $[Cu_2Cl_2(tscac)_2]_2$ indicates the existence of weak hydrogen bonding (N−H···Cl) as seen in the crystal structure.

(2) The $\nu_{C=N}$ band at 1594 cm^{-1} in the free ligand is shifted to lower frequency in the complexes {1546 cm^{-1} in $[Cu(tscac)_2]Cl$ and 1555 cm^{-1} in $[Cu_2Cl_2(tscac)_2]_2$}. This shift supports the coordination of copper to the imine nitrogen.[8] The bands between 1400−1500 cm^{-1} in the spectra of the free ligands and the complexes can be assigned to the ν_{C-N} band.

(3) The absorptions at 789, 754 and 744 cm^{-1} can be assigned to the C=S stretching in the free ligand, $[Cu(tscac)_2]Cl$ and $[Cu_2Cl_2(tscac)_2]_2$ respectively. These shifts to lower energy in the complexes indicate a weaker C=S bond upon coordination with copper. A comparison of the vibrational frequencies in the tscac ligand and the complexes is shown in Table 2.

Table 2. Comparison of some vibration frequencies and bond lengths in tscac and the complexes

Compound	C=S		C=N	
	$\tilde{\nu}$ (cm^{-1})	Distance (Å)	$\tilde{\nu}$ (cm^{-1})	Distance (Å)
tscac	789 s	1.690[2]	1594 s	1.292[2]
$[Cu(tscac)_2]Cl$	752 s	1.6900(19) 1.6988(17)	1546 s	1.289(2) 1.285(2)
$[Cu_2Cl_2(tscac)_2]_2$	744 s	1.708(4) 1.713(4)	1555 s	1.290(5) 1.280(5)

Both complexes are ESR silent and display no d-d electronic spectra, consistent with the presence of Cu^I species.

The reactions at the anode were established by the weight loss of the copper sheet, which was weighed before and after the reaction. The electrochemical efficiency of 0.96 and 1.14 found for both complexes indicates that the anode material loses one electron per atom. The colorless gas observed at the cathode is formed as a result of the reduction of hydrogen ion either from the ligand or the acid. Mabrouk and co-workers[9] have suggested that in the electrochemical synthesis of metal complexes with thiosemicarbazide the ligand loses a proton and becomes negatively charged. If the reactions in this study occurred as described above, the number of tscac protons in the complexes should not be equal to the number of protons in the free ligand. The ^1H NMR spectra, however, show an equal number of protons in the free ligand and the complexes. In addition, the preparative results show that hydrochloric acid must be added to the reaction mixture otherwise the electrolysis will not occur. Therefore the hydrogen gas must be formed from the protons in the hydrochloric acid not in the ligand.

Conclusion

It can be concluded from the electrolysis data (see Exp. Sect.) that the electrolysis of copper in the presence of acetonethiosemicarbazone occurs as follows [Equation (1) and (2)]:

$$\text{for } 1:2 \text{ adduct } ([Cu(tscac)_2]Cl)$$

$$Cu + 2\,Tscac + Cl^-_{(aq)} \longrightarrow \text{complex } \mathbf{1} + e^- \qquad (1)$$

$$\text{and} \quad \text{for } 1:1 \text{ adduct } ([Cu_2(tscac)_2Cl_2]_2)$$

$$4\,Cu + 4\,Tscac + 4\,Cl^- \longrightarrow \text{complex } \mathbf{2} + 4\,e^- \qquad (2)$$

Alternatively the complexes may be prepared by chemical synthesis as outlined below

Experimental Section

Materials and Instruments: All chemicals are commercially available (BDH Co., Carlo Erba, Merck Co., Fluka, May & Baker Co. Ltd., Mallinckvodt Co.) and used without further purification. The infrared spectra were measured as KBr discs on a Perkin−Elmer Model SYSTEM 2000 spectrophotometer. ^1H NMR spectra were recorded on a JEOL Model JNM-A500 FT NMR 500 MHz spectrometer with deuterated dimethyl sulfoxide (DMSO) as solvent and internal standard. X-ray analyses were carried out using a Siemens Smart CCD diffractometer.

The electrochemical cell consists of a platinum cathode and the sacrificial copper anode immersed in an ammonium chloride solution containing acetonethiosemicarbazone. The complexes were prepared using the method described by Mabrouk and coworkers[9] with slight modification. After each electrolysis the electrochemical efficiency(E_f) was determined. The electrochemical efficiency is defined as mol of metal dissolved per Faraday of electricity. The amount of electricity used for each experiment in this study is equal to 72 coulomb or 7.5×10^{-4} Faradays. Theoretically, this amount of electricity dissolves Cu^+ 7.5×10^{-4} mol or Cu^{2+} 3.75×10^{-4} mol. Therefore, the E_f for Cu^+ and Cu^{2+} must be close to 1 and 0.5 $mol{\cdot}F^{-1}$. This means that after electrolysis the E_f for one-electron transfer must be close to 1 and for two-electron transfer to 0.5. The variation of voltage, current and time was performed in order to determine the optimum electrolysis conditions. The electrochemical conditions described below are the optimum conditions for each complex.

Acetonethiosemicarbazone (tscac): The ligand was prepared using the method described by Sunner[10] with a slight modification. Thiosemicarbazide (2 mmol) was added to acetone (50 mL) and the mixture was heated and stirred until a white precipitate had formed. The compound was collected (yield 98%) and recrystallized from a mixture of water and acetone. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta = 1.89$ (s, 3 H, CH_3), 1.90 δ (s, 3 H, CH_3), 7.49 (br, 1 H, NH_2), 7.95 (br, 1 H, NH_2) and 9.87 (br, 1 H, NH) ppm.

Complex 1 by Chemical Synthesis: In this synthesis the mol ratio of Cu:tscac is 1:2. A 6 M solution of NH_3 was added to a solution of CuCl (1.5 mmol in 6 M HCl) until the pH of the solution was 4−5. After adding thiosemicarbazone (3.0 mmol in 50 mL acetone) dropwise with stirring at room temperature, the reaction mixture formed two layers. Concentrated ammonium chloride solution was then added to the two layers until a single layer formed. The reaction mixture became pale yellow and was then filtered. Upon slow evaporation for 12−24 hours at room temperature, yellow octahedral crystals were formed. The product was collected, washed with water and acetone and dried in an oven at 60−70 °C. Yield: 40% (0.109 g). The infrared spectrum shows the presence of the tscac ligand in the yellow product. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta = 2.00$ (m, 12 H, CH_3), 7.63 and 8.86 (br, 4 H, NH_2), 10.92 (s, 2 H, NH).

Complex 2 by Chemical Synthesis: This complex was prepared in a similar procedure to that described above, but using a mol ratio of Cu:tscac of 1:1. After slow evaporation of the solvent from the pale yellow solution for 1−2 days at room temperature, colorless needles were formed. The product was filtered, washed with water and acetone, and dried in an oven at 60−70 °C. Yield: 38% (0.132 g). The infrared spectrum shows the presence of tscac in the product. This complex turns green when exposed to air for several weeks. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta = 2.00$ (m, 12 H, CH_3), 7.98 and 8.47 (s, 4 H, NH_2), 10.31 and 11.41 (s, 2 H, NH).

Complex 1 by Electrochemical Synthesis: The electrochemical oxidation of a copper anode in an acidic solution containing acetone (50 mL), 6 M HCl (0.5 mL), acetonethiosemicarbazone (1.5 mmol) and ammonium chloride (0.5 g) for half hour at 4.5 V and 40 mA led to the dissolution of 47.4 mg of copper as the Cu^I ion. The reaction mixture became pale yellow and was then filtered to remove insoluble impurities. The solvent was then slowly evaporated from the filtrate at room temperature. After 6 hours, yellow crystals formed. These were then filtered off, washed with water and acetone successively and dried in an oven at 60−70 °C. Yield: 98% (0.266 g). The infrared spectrum shows the presence of tscac in the yellow crystals. The electrochemical efficiency of this reaction was evaluated (see above).

Complex 2 by Electrochemical Synthesis: The electrochemical oxidation of a copper anode in an acidic solution containing acetone (50 mL), 6 M HCl (0.5 mL), acetonethiosemicarbazone (1.5 mmol) and ammonium chloride (0.5 g) for one hour at 3.5 V and 40 mA led to the dissolution of 94.8 mg of copper as the Cu^I ion. The reaction mixture was pale yellow solution and then was filtered to remove the impure particles. The reaction mixture became pale yellow and was then filtered to remove insoluble impurities. The solvent was then slowly evaporated from the filtrate at room temperature. After 8 hours, pale yellow crystals had formed. These were then filtered off, washed with water and acetone successively and dried in an oven at 60−70 °C). Yield: 69% (0.273 g). The infrared spectrum shows the presence of coordination between Cu and tscac. The electrochemical efficiency of this reaction was evaluated (see above). This complex did not give a suitable crystal for the collection of X-ray diffraction data.

X-ray Crystallographic Study: The diffraction data for all complexes with appropriate size crystals were collected at 298(2) K on a 1 K Bruker Smart CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). For data collection and data integration, the SMART and SAINT programs were used[11] and empirical absorption correction was performed with the program SADABS.[12] The structures were solved by direct methods using the SHELXTL program system[13] for all complexes and were refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. For all complexes the hydrogen atoms were located from a Fourier difference map and refined. Crystal parameters and refinement results for all complexes showed that the complexes prepared by both methods resulted in the same crystal structure. Crystal data and refinement results of complexes **1** and **2** prepared by chemical method are listed in Table 3.

Table 3. Crystallographic data

	1	**2**
Complex	[Cu(tscac)$_2$]Cl	[Cu$_2$Cl$_2$(tscac)$_2$]$_2$
Formula	$C_8H_{18}ClCuN_6S_2$	$C_{16}H_{36}Cl_4Cu_4N_{12}S_4$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a [Å]	11.3795(1)	8.0512(2)
b [Å]	11.5664(1)	15.8665(3)
c [Å]	12.1246(2)	13.6949(3)
α, β, γ [°]	90, 90, 90	90, 94.212(1), 90
V [Å^3]	1595.84(3)	1744.72(7)
Z	4	2
D_m [g cm^{-3}], flotation	1.506	1.748
D_c [g cm^{-3}]	1.504	1.753
μ [mm^{-1}]	1.790	2.981
$2\theta_{max}$ [°]	56.65	61.15
No. reflections measured	10818	12546
Independent	3918	5006
R	0.0225	0.0553
R_w	0.0518	0.0809

CCDC-182401 (**1**) and -182402 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] M. A. Ali, S. E. Livingstone, *Coord. Chem. Rev.* **1974**, *13*, 101−132.

[2] M. J. M. Campbell, *Coord. Chem. Rev.* **1975**, *15*, 279−319.

[3] D. Chattopadyay, S. K. Majumdar, P. Lowe, C. H. Schwalbe, S. K. Chattopadhyay, S. Ghosh, *J. Chem. Soc., Dalton Trans.* **1991**, *8*, 2121−2124.

[4] M. B. Ferrari, G. G. Fava, P. Tarasconi, R. Albertini, S. Pinelli, R. Starcich, *J. Inorg. Biochem.* **1994**, *53*, 13−25.

[5] J. V. Martinez, R. A. Toscano, J. R. Ortiz, *Polyhedron* **1995**, *14*, 579−583.

[6] M. A. Ali, K. K. Dey, M. Nazimuddin, F. E. Smith, R. J. Butcher, J. P. Jasinski, J. M. Jasinski, *Polyhedron* **1996**, *15*, 3331−3339.

[7] J. G. Tojai, J. G. Jaca, R. Cortes, T. Rojo, M. K. Urtiaga, M. I. Arriortua, *Inorg. Chim. Acta* **1996**, *249*, 25−32.

[8] M. B. Ferrari, G. G. Fava, E. Leporati, G. Pelosi, R. Rossi, P. Tarasconi, R. Albertini, A. Bonati, P. Lunghi, S. Pinelli, *J. Inorg. Biochem.* **1998**, *70*, 145−154.

[9] H. E. Mabrouk, A. A. Fl-Asmy, T. Y. Al-Ansi, M. Mounir, *Bull. Soc. Chim. Fr.* **1991**, *128*, 309−313.

[10] S. Sunner, *Kgi. Fysiograf. Sällskap. Lund. Förh.* **1948**, *18*, 139−148.

[11] SMART, Data Collection Software, Version 4.0 and SAINT, Data Integration Software, Version 4.0; Bruker AXS, Inc., Madison, WI, **1997**.

[12] G. M. Sheldrick, *SADABS, Program for Empirical Absorption of Göttingen.* **1996**.

[13] G. M. Sheldrick, *SHELXTL version 5.1*, University of Göttingen, Göttingen, Germany, **1993**.

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