PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 975–979

POLYHEDRON

www.elsevier.com/locate/poly

Two new polymeric cadmium(II) complexes containing end-to-end bridging azido or thiocyanato ligands with different topologies

Mohamed A.S. Goher [a,*], Franz A. Mautner [b], Afaf K. Hafez [a],
Morsy A.M. Abu-Youssef [a], Christian Gspan [b], Ahmed M.-A. Badr [a]

[a] *Department of Chemistry, Faculty of Science, Alexandria University, PO Box 426 Ibrahimia, Alexandria 21321, Egypt*
[b] *Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Rechbauerstr. 12, A-8010 Graz, Austria*

Received 19 August 2002; accepted 10 January 2003

Abstract

Two new polymeric cadmium(II) complexes; $[Cd(3,5\text{-DMP})_2(N_3)_2]$ (**1**) and $[Cd(4\text{-Brpy})_2(NCS)_2]$ (**2**), where 3,5-DMP = 3,5-dimethylpyridine and 4-Brpy = 4-bromopyridine, have been synthesized and characterized. IR spectral data suggest end-to-end bridging azido and thiocyanato ligands. X-ray crystal structure determination has shown the 1-D complex **1** to contain each cadmium octahedrally coordinated by two double μ(1,3)-bridging azides and the other two sites are occupied by two pyridine ligands in a *cis*-arrangement. The Cd–Cd distances in the $Cd_2(N_3)_2$ eight membered rings are 5.142(2) and 5.152(2) Å, the azide ligands are almost symmetrical and linear [N–N distances: 1.167(5)–1.182(5) Å; $\angle$NNN = 176.7(4)° and 177.6(4)°]. In complex **2** each octahedrally cadmium atom is coordinated by two *trans* pyridine ligands and two *trans* nitrogen or sulfur atoms from four μ(N,S) bridging thiocyanato groups. The other end atoms of these four thiocyanato ligands bind four different cadmium atoms giving a 2-D layer structure.

Keywords: Cadmium(II) azido and thiocyanato complexes; Pyridine derivative complexes; Preparation; Spectra; Crystal structures

1. Introduction

Charged ligands like azide or thiocyanate are used to bridge metal centers which gives complexes of anomalous architectures with important physical properties such as supramolecular chemistry [1] and molecular magnetism [2]. The azide and thiocyanate anions are versatile ligands that can bridge metal centers either by end-to-end (μ-1,3 or μ-N,S) or end-on (μ-1,1 or μ-NN, μSS) fashion, both possibilities being structurally characterized for transition metal complexes [3–8]. When the azide group acts as a bridging ligand with an end-on coordination mode the resulting binuclear complex usually shows ferromagnetic behavior, whereas end-to-end coordination results in antiferromagnetic behavior [6].

Although a substantial array of azido complexes of manganese(II) [9], nickel(II) [10] and copper(II) [11] of pyridine derivatives and other ligands have been synthesized and characterized, the corresponding cadmium(II) complexes are still very few [12–17]. As part of our investigation on rational design and preparation of metal azides, we have recently reported a number of cadmium(II) azido coordination polymers with such pyridine derivative ligands [18]. We now report for two new polymeric cadmium(II) azido and thiocyanato complexes having the same bridging mode of the azide and thiocyanate groups but different cadmium pseudohalide topologies.

2. Experimental

3,5-Dimethylpyride (3,5-DMP) and 4-bromopyridine (4-Brpy) were purchased from Aldrich company and other chemicals are of analytical grade quality.

---

* Corresponding author. Fax: +2-3-391-1794.
E-mail addresses: masidahmed@hotmail.com (M.A.S. Goher), mautner@ptc.tu-graz.ac.at (F.A. Mautner).

0277-5387/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0277-5387(03)00022-6

Caution: metal azide complexes are potentially explosives. Only a small amount of material should be prepared and should be handled with caution.

2.1. *Preparation of polymeric [Cd(3,5-DMP)$_2$ (N$_3$)$_2$] (**1**)*

Complex **1** was prepared by mixing $3CdSO_4 \cdot 8H_2O$ (0.5 g, 1.95 mmol) in water (20 ml) with 3,5-DMP (0.47 g, 4.40 mmol), followed by a dropwise addition of 5 ml aqueous solution of NaN_3 (0.325 g, 5 mmol). The final mixture was allowed to stand several days at room temperature (r.t.) to obtain colorless crystals. Yield: approximately 50%. $C_{14}H_{18}CdN_8$ (410.76). Analytical data: Found (Calc.): C, 40.8 (40.9); H, 4.3 (4.4); Cd, 27.6 (27.4); N, 27.3 (27.3)%.

2.2. *Preparation of polymeric [Cd(4-Brpy)$_2$(NCS)$_2$]$_n$ (**2**)*

This complex was prepared by mixing $3CdSO_4 \cdot 8H_2O$ (0.5 g, 1.95 mmol) in water (15 ml) with 4-Brpy (1.00 g, 6.33 mmol) in ethanol (10 ml), followed by a dropwise addition of 5 ml aqueous solution of NaNCS (0.40 g, ~ 5 mmol). Colorless crystals were obtained by allowing the final mixture to stand over several days in open air. Yield: approximately 50%. $C_{12}H_8Br_2CdN_4S_2$ (544.56). Analytical data: Found (Calc.): C, 26.4 (26.5); H, 1.5 (1.5); Cd, 20.8 (20.6); N, 10.2 (10.3)%.

2.3. *Physical measurements*

The experimental procedures and instruments used for physical measurements were described previously [18].

2.4. *X-ray crystallography*

A modified STOE four circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 30 reflections in the θ range 10.2°–15.4° (**1**) and 30 reflections in the θ range 10.8°–17.2° (**2**). Data were collected at 90(2) K using graphite crystal-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz-polarization effects, for intensity decay (intensities of three standard reflections dropped during data collection by 34% and 7% for compounds **1** and **2**, respectively), and for absorption. Crystallographic data and processing parameters are given in Table 1. The structures were solved by direct methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The program DIFABS [19] and SHELXTL/PC program package [20] were used for computations. Selected bond distances and bond angles are given in Tables 2 and 3.

Table 1
Crystallographic data and processing parameters

Compound	**1**	**2**
Empirical formula	$C_{14}H_{18}CdN_8$	$C_{12}H_8Br_2CdN_4S_2$
Formula mass	410.76	544.56
Color	colorless	colorless
System	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.638(4)	7.653(3)
b (Å)	7.574(2)	9.689(2)
c (Å)	16.362(6)	11.005(4)
β (°)	100.42(3)	98.35(3)
V (Å^3)	1662.2(9)	807.4(5)
Z	4	2
μ (Mo Kα) (mm^{-1})	1.326	6.556
Normal transmission factors	1.000–0.572	1.000–0.430
D_{calc} (Mg m^{-3})	1.641	2.240
Approximate crystal size (mm)	0.35 × 0.18 × 0.17	0.22 × 0.12 × 0.10
θ Range of data collection (°)	2.97–25.99	2.81–25.01
Reflections collected	3824	1666
Independent reflections	2994 [$R_{int} = 0.0253$]	1267 [$R_{int} = 0.0280$]
Parameters	212	97
Goodness-of-fit on F^2	1.100	1.183
R_1/wR_2	0.0355/0.0904	0.0305/0.0949
Weighting factors: a/b [a]	0.0324/1.9347	0.0000/4.4639
Largest peak and hole (e Å^{-3})	0.405 and −0.509	0.612 and −0.552

[a] $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

The reactions between cadmium(II) ions and 3,5-DMP and 4-Brpy in aqueous/alcoholic medium and in presence of N_3^- or SCN^- ions afforded complexes **1** and **2**. Both complexes are insoluble in non-polar solvents, e.g. benzene, CCl_4, etc. and in polar solvents, e.g. H_2O, MeOH, EtOH, acetone, etc. indicating their polymeric nature. Complex **1** is slightly soluble in DMSO whereas **2** soluble. The H NMR spectrum of **2** in this solvent suggests that the thiocyanate groups are completely substituted by DMSO. The same result was obtained from ^{13}C NMR, indicating that DMSO is stronger bonded to Cd(II) than SCN^- groups. On the other hand, mass spectrum of **2** revealed that complex **2**

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

Bond lengths			
Cd(1)···Cd(1a)	5.152(2)	Cd(1)···Cd(1b)	5.142(2)
Cd(1)–N(1)	2.312(3)	Cd(1)–N(2)	2.325(3)
Cd(1)–N(13)	2.329(3)	Cd(1)–N(23a)	2.342(3)
Cd(1)–N(11)	2.345(3)	Cd(1)–N(21)	2.362(3)
N(11)–N(12)	1.172(5)	N(12)–N(13b)	1.181(4)
N(21)–N(22)	1.167(5)	N(22)–N(23)	1.182(5)
Bond angles			
N(1)–Cd(1)–N(2)	103.15(11)	N(1)–Cd(1)–N(13)	88.90(11)
N(2)–Cd(1)–N(13)	85.42(11)	N(1)–Cd(1)–N(23a)	85.60(11)
N(2)–Cd(1)–N(23a)	88.89(11)	N(13)–Cd(1)–N(23a)	170.99(11)
N(1)–Cd(1)–N(11)	169.86(12)	N(2)–Cd(1)–N(11)	85.28(12)
N(13)–Cd(1)–N(11)	97.48(12)	N(23a)–Cd(1)–N(11)	88.98(12)
N(1)–Cd(1)–N(21)	88.03(12)	N(2)–Cd(1)–N(21)	167.49(12)
N(13)–Cd(1)–N(21)	89.27(12)	N(23a)–Cd(1)–N(21)	97.66(12)
N(11)–Cd(1)–N(21)	84.20(12)	N(12)–N(11)–Cd(1)	120.2(3)
N(11)–N(12)–N(13b)	177.6(4)	N(12b)–N(13)–Cd(1)	120.2(3)
N(22)–N(21)–Cd(1)	121.5(3)	N(21)–N(22)–N(23)	176.7(4)
N(22)–N(23)–Cd(1a)	118.0(3)		

Symmetry codes; (a) $-x+2, -y, -z$; (b) $-x+2, -y+1, -z$.

Table 3
Selected bond lengths (Å) and angles (°) for (**2**)

Bond lengths			
Cd(1)···Cd(1a)	6.173(2)	Cd(1)–N(1b)	2.316(5)
Cd(1)–N(2c)	2.350(5)	Cd(1)–S(6)	2.704(2)
Br(1)–C(4)	1.901(7)	S(6)–C(1)	1.661(7)
C(1)–N(1)	1.148(8)		
Bond angles			
N(1b)–Cd(1)–N(2c)	91.0(2)	N(1a)–Cd(1)–S(6c)	92.64(14)
N(2c)–Cd(1)–S(6c)	90.33(13)	C(1)–S(6)–Cd(1)	99.1(2)
N(1)–C(1)–S(6)	178.5(6)	C(1)–N(1)–Cd(1d)	159.2(5)

Symmetry codes; (a) $-x+1/2, y-1/2, -z$; (b) $x-1/2, -y+1/2, z$; (c) $-x, -y, -z$; (d) $-x+1/2, y+1/2, -z$.

decomposes to SCN^-, 4-Brpy, Br, py, and some small molecular weight fragments.

3.1. Structures

Fig. 1 illustrates the principle features of complex **1**, selected bond distances and bond angles are collected in Table 2. The structure consists of neutral chains of cadmium atoms linked by azido bridges, placed along the [010] direction (Fig. 2). The forming octahedral coordination around the cadmium atoms consists of two 3,5-dimethylpyridine ligands coordinated via the pyridine nitrogen atom and four azide bridges which act as end-to-end (μ-1,3) double bridges with the two neighboring cadmium atoms. The two sets of μ-1,3 bridges are not equivalent, giving an alternating system. In this structure, the N–N bond distances are practically symmetrical, [N–N = 1.172(5), 1.181(4) and 1.167(5), 1.182(5) Å; ∠NNN = 177.6(4)° and 176.7(4)°]. The bond angles [Cd(1)–N(11)–N(12) and Cd(1)–N(13)–N(12A) are both 120.2(3)°, Cd(1)–N(21)–N(22) and Cd(1)–N(23B)–N(22B) are 121.5(3)° and 118.0(3)°, respectively], lie in the normal range [21] found for related μ-1,3 compounds. The eight-membered $M_2(NNN)_2$ rings of double μ-1,3 bridging azido ligands have been observed in structures of several metal azido complexes, e.g. $[Cu(4\text{-picoline})_2(N_3)_2]_n$ [22], *cis*-$[Mn(2,2'\text{-bpy})(N_3)_2]_n$ [21,23]. The Cd–Cd distances for A and B rings are 5.152(2) and 5.142(2) Å, respectively, whereas the minimum interchain distance is 9.156(3) Å, due to the large size of the 3,5-DMP ligands which efficiently isolate the chains. It is worthy to point out that the cadmium skeleton consists of zigzag chains due to the *cis*-coordination of the bridges with Cd(1A)···Cd(1)···Cd(1B) angle of 94.7(2)° (Fig. 2).

The structure of complex **1** is very similar to the corresponding complex $[Mn(3,5\text{-DMP})_2(N_3)_2]_n$ (**3**), which also crystallizes in the $P2_1/n$.space group [24]. The bond lengths and angles for **3** are: Mn(1)–N(1) = 2.251(3), Mn(1)–N(2) = 2.271(3), Mn(1)–N(11) = 2.225(3), Mn(1)–N(13a) = 2.252(3), Mn(1)–N(21) = 2.220(3) and Mn(1)–N(23b) = 2.245(3) Å; Mn(1)–N(21)–N(22) = 122.9(3)° and Mn(1b)–N(23)–N(22) = 124.8(3)°, Mn(1)–N(11)–N(12) and Mn(1b)–N(13a)–N(12a) = 121.9(2)° and 125.8(2)°, respectively; the Mn···Mn intrachain distances are 5.159(1) and 5.140(1) Å, for A and B rings, respectively.

The atom labeling scheme for complex **2** is shown in Fig. 3. The structure consists of an extended 2-D layer of octahedrally coordinated centrosymmetric cadmium atoms bridged by means of μ-1,3 thiocyanato-N,S ligands. Each cadmium atom has two 4-bromopyridine ligands in *trans* arrangement and two *trans* nitrogen atoms and two sulfur atoms from four thiocyanato ligands. The Cd–N(4-Brpy) distance is 2.350(5), Cd–N(NCS) = 2.316(5) and Cd–S(SCN) = 2.704(2) Å. These values are little longer than corresponding values in $[Cd(\text{picolinato})(NCS)]_n$ [Cd–N(pic) = 2.315(4), Cd–N(NCS) = 2.275(4) and Cd–S = 2.594(2) Å] [12] containing also μ-1,3 thiocyanato ligands, but match those reported in the structure of $[Cd(SCN)_2(4\text{-abaH})_2]_n$ (abaH = 4-aminobenzoic acid) [Cd–N(NCS) = 2.305(4) and 2.278(2) and Cd–S(SCN) = 2.682(2) and 2.693(4) Å] [17]. Each of the four thiocyanato ligands acts as a μ-1,3 (μ-N,S) bridge with each one of the neighboring cadmium atoms giving an extended two-dimensional layer (Fig. 4). Bond angles Cd(1)–N(1)–C(1) = 159.2(5)° and Cd(1)–S(1)–C(1) = 99.1(2)° agree with corresponding values reported in polymeric $[Cd(\text{picolinato})(NCS)]_n$ [Cd–N–C = 165.4(4)° and Cd–S–C = 97.9(2)° [12].

3.2. Infrared spectra

The IR spectrum of **1** exhibits a very strong band at 2039 cm^{-1} due to $\nu_{as}(N_3)$. This band is very similar to

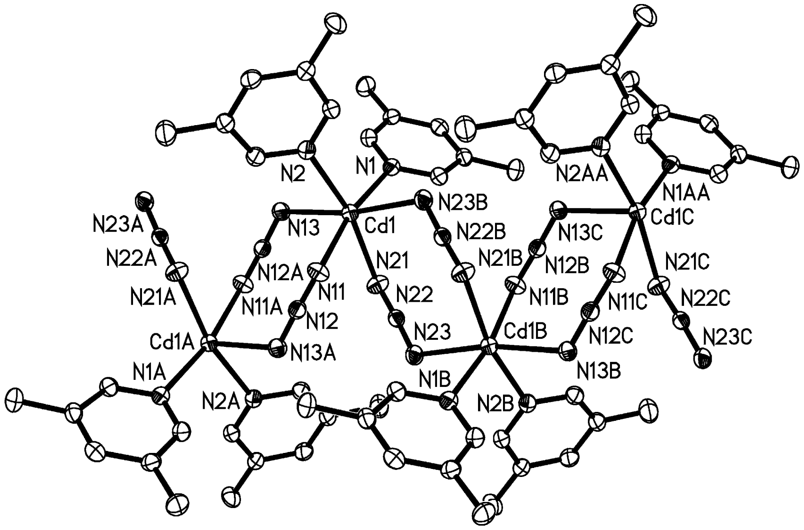

Fig. 1. Perspective view with atom labeling scheme within a chain of $[Cd(3,5\text{-dimethylpyridine})_2(N_3)_2]_n$ (**1**).

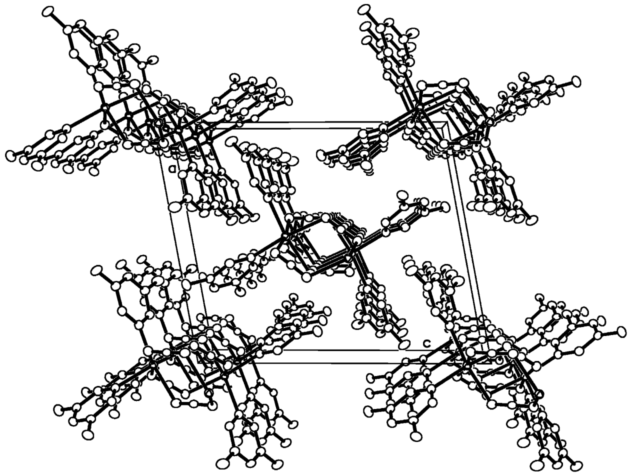

Fig. 2. $[Cd(3,5\text{-dimethylpyridine})_2(N_3)_2]_n$ (**1**); packing view along *b*-axis of unit cell.

that observed in $[Cd(py)_2(N_3)_2]_n$ containing μ-1,3 bridging azido groups [13]. Thus the IR spectrum suggests that the azides in complex **1** are of the type μ-1,3 and symmetrical. We could not locate any absorption band due to $\nu_s(N_3)$ in the region 1280–1350 cm^{-1}, which strongly confirms the symmetrical nature of the azide ligands in this complex.

The IR spectrum of solid complex **2** shows one very strong and sharp band at 2096 cm^{-1} due to the ν(CN) mode, in addition to medium to strong bands at 779 and 765 cm^{-1} related to ν(CS). Bridging N,S-thiocyanato groups are expected to exhibit two ν(CN) bands above and below 2000 cm^{-1} as well as two ν(CS) bands [25–29]. While the appearance of two ν(CS) bands in addition of two δ(NCS) at 453 and 408 cm^{-1} is suggestive of μ-1,3-thiocyanato-N,S, the single ν(CN) band is not consistent with the X-ray structure result of the complex. However, the appearance of a single ν(CN) around 2000 cm^{-1}, is not uncommon and has been reported in many μ(N,S)-thiocyanato complexes [7,30,31].

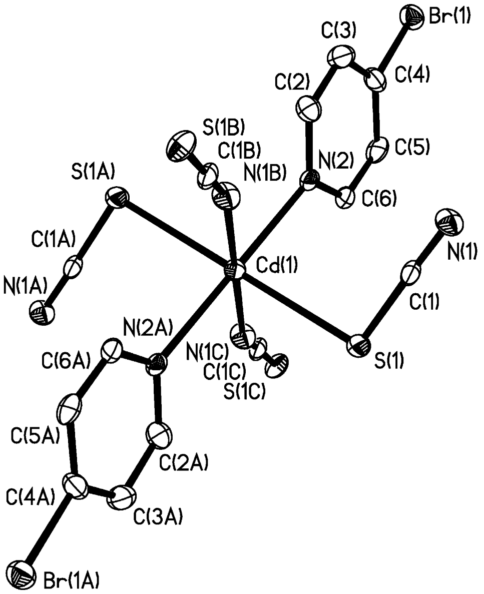

Fig. 3. Coordination figure and atom labeling scheme of $[Cd(4\text{-bromopyridine})_2(NCS)_2]_n$ (**2**).

4. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition numbers: CCDC-191342 and CCDC-191343 for **1** and **2**, respectively.

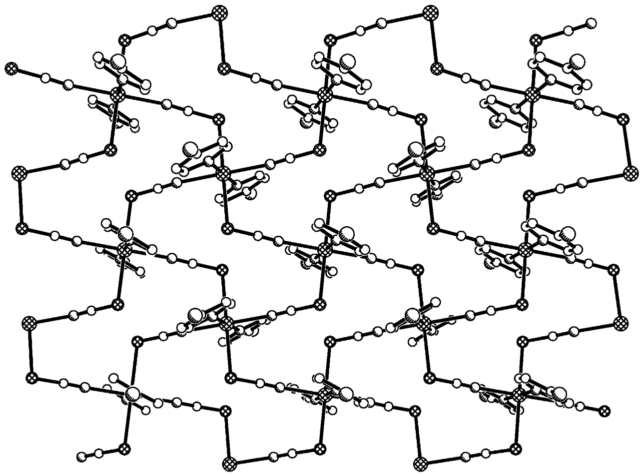

Fig. 4. View onto a layer of the 2-D system [Cd(4-bromopyridine)$_2$(NCS)$_2$]$_n$ (**2**). The layers are oriented parallel to the *ab*-plane of unit cell.

Acknowledgements

The authors thank Professor C. Kratky, Professor F. Belaj (University Graz, Austria) and Professor L. Öhrström (Chalmers Technical University, Göteborg, Sweden) for use and kind help with various experimental equipments.

References

[1] J.M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.

[2] O. Kahn (Ed.), Molecular Magnetism, a Supramolecular Function, Kluwer, Dordrecht, 1996.

[3] H. Zhang, X. Wang, K. Zhang, B.K. Gao, Coord. Chem. Rev. 183 (1999) 157.

[4] Z. Dori, R.F. Ziolo, Chem. Rev. 73 (1973) 247.

[5] J. Ribas, M. Monfort, B.K. Ghosh, X. Solans, M. Font-Bardia, J. Chem. Soc., Chem. Commun. (1995) 2375.

[6] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.

[7] (a) M.A.S. Goher, L.A. Al-Shatti, F.A. Mautner, Polyhedron 16 (1997) 889;
(b) I. Solaculo, D. Sandulescu, C. Dragulescu, Rev. Roum. Chem. 19 (1974) 415;
(c) J.H. Takamoto, B. Hutchinson, Inorg. Chem. 12 (1973) 705.

[8] (a) E. König, K.J. Watson, Chem. Phys. Lett. 6 (1970) 157;
(b) R.E. March, Acta Crystallogr., Sect. B 51 (1995) 897.

[9] M.A.M. Abu-Youssef, M. Drillon, A. Escuer, M.A.S. Goher, F.A. Mautner, R. Vicente, Inorg. Chem. 39 (2000) 5022 (and references therein).

[10] M.A.S. Goher, A. Escuer, F.A. Mautner, N.A. Al-Salem, Polyhedron 21 (2002) 1871 (and references therein).

[11] A. Escuer, M.A.M. Goher, F.A. Mautner, R. Vicente, Inorg. Chem. 39 (2000) 2107 (and references therein).

[12] F.A. Mautner, M.A.M. Abu-Youssef, M.A.S. Goher, Polyhedron 16 (1997) 235.

[13] (a) I. Agrell, Acta Chem. Scand. 21 (1967) 2647;
(b) I. Agrell, Acta Chem. Scand. 24 (1970) 3575.

[14] W. Clegg, H. Krischner, A.I. Saracoglu, G.M. Sheldrick, Z. Kristallogr. 161 (1982) 307.

[15] H. Krischner, C. Kratky, H.E. Maier, Z. Kristallogr. 161 (1982) 225.

[16] N. Mondal, M.K. Saba, S. Mitra, V. Gramlich, J. Chem. Soc., Dalton Trans. (2000) 3218.

[17] H.-J. Chen, X.-M. Chen, Inorg. Chim. Acta 329 (2002) 13.

[18] M.A.S. Goher, F.A. Mautner, M.A.M. Abu-Youssef, A.K. Hafez, A.M.A Badr, J. Chem. Soc., Dalton Trans., (2002) 3309.

[19] N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158.

[20] SHELXTL/PC v.5.03, Siemens Analytical Automation Inc., Madison, WI, 1995.

[21] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, Coord. Chem. Rev. 193–195 (1999) 1027.

[22] M.A.S. Goher, F.A. Mautner, Cryst. Res. Technol. 27 (1992) 817.

[23] R. Cortes, K. Urtiaga, L. Lezama, M.L. Rodriguez, M.I. Arriortua, T. Rojo, Inorg. Chem., submitted for publication.

[24] M.A.M. Abu-Youssef, A. Escuer, D. Gatteschi, M.A.S. Goher, F.A. Mautner, R. Vicente, Inorg. Chem. 38 (1999) 5116.

[25] (a) P.C.H. Mitchell, R.J.P. Williams, J. Chem. Soc. (1960) 1912.;
(b) A. Tramer, J. Chem. Phys. 59 (1962) 232.

[26] J. Lewin, R.S. Nyholm, P.N. Smith, J. Chem. Soc. (1961) 4590.

[27] A. Subatini, I. Bertini, Inorg. Chem. 4 (1965) 959.

[28] (a) R.J.H. Clark, C.S. Williams, Spectrochim. Acta 22 (1966) 1081;
(b) M. Aslam, W.H.S. Assai, Inorg. Nucl. Chem. Lett. 7 (1971) 96.

[29] M.A.S. Goher, Coll. Czech. Chem. Commun. 42 (1977) 1478.

[30] (a) J. Chatt, L.A. Duncanson, F.A. Hart, P.G. Owston, Nature 178 (1956) 997;
(b) J. Chatt, L.A. Duncanson, F.A. Hart, P.G. Owston, Nature 181 (1958) 43.

[31] P.G. Owston, J.M. Rowe, Acta Crystallogr. 13 (1960) 253.