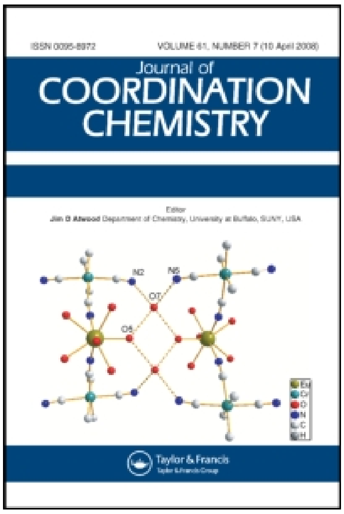

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A cyanide-containing cobalt(III) complex [Co(phen)$_2$(CN)$_2$][Co(phen)(CN)$_4$]·4.5H$_2$O: hydrothermal synthesis, crystal structure and spectroscopic properties

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A cyanide-containing cobalt(III) complex $[Co(phen)_2(CN)_2][Co(phen)(CN)_4] \cdot 4.5H_2O$: hydrothermal synthesis, crystal structure and spectroscopic properties

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A cyanide-containing cobalt(III) complex, $[Co(phen)_2(CN)_2][Co(phen)(CN)_4] \cdot 4.5H_2O$ (**1**: phen = 1,10-phenanthroline) has been synthesized by hydrothermal techniques and characterized by elemental analyses, IR spectroscopy, UV–vis spectroscopy and single-crystal X-ray diffraction methods. The complex is triclinic, space group $P\bar{1}$, with $a = 11.0047(16)$, $b = 12.9587(19)$, $c = 15.076(2)$ Å, $\alpha = 100.060(2)$, $\beta = 102.061(2)$, $\gamma = 91.803(2)^\circ$, $V = 2065.0(5)$ Å^3, $Z = 2$, and R_1 $[I > 2\sigma(I)] = 0.0481$. The molecular unit of **1** consists of a cation/anion pair with interstitial water molecules in the crystal lattice. The combination of coordinative, hydrogen bonding and π–π stacking interactions results in the stabilization of a supramolecular solid-state architecture.

Keywords: Cyanide-containing; Cobalt(III) complex; Hydrothermal synthesis; Crystal structure

1. Introduction

Transition metal cyanide systems [1] have been extensively investigated due to their structural richness and various physical properties which give rise to a large range of potential applications in composite inorganic–organic hybrid materials [2], catalysts [3], inclusion compounds [4] and molecular-based magnets [5]. Although the majority of synthetic procedures of these systems still follow conventional solution routes, increasing interest has been paid to the less conventional hydrothermal techniques. In this regard, various groups (Zubieta's [6] for example) have contributed significantly by synthesizing and characterizing cyanide-bridged extended networks. Most of these reported complexes focus on homometallic cyanide-bridged copper(I) extended systems in which CuCN and/or MCN (M = Na, K) act as a source of cyanide groups [6–12]. Recently, Colacio [13] and others [14–17] have shown that cyanide-bridged heterobimetallic and homometallic coordination complexes can also be constructed through hydrothermal reactions by using the hexacyanoferrate(III) or

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hexacyanocobaltate(III) anions as precursors. In an attempt to use hydrothermal synthesis methods to prepare new coordination compounds, we have decided to use the octacyanotungsten(IV) anions as the source of cyanide. In this article, we present the hydrothermal preparation, structural characterization and spectroscopic properties of a new cyanide-containing cobalt(III) complex incorporating cation/anion pair systems with lattice water, $[Co(phen)_2(CN)_2][Co(phen)(CN)_4] \cdot 4.5H_2O$ (phen = 1,10-phenanthroline).

2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 instrument. IR spectra in the 4000–400 cm^{-1} region were recorded on a Tensor 27 spectrophotometer using KBr pellets. Electronic spectra were measured on a JASCO V-570 spectrophotometer at room temperature using dimethylformamide (DMF) as the solvent.

2.2. *Materials and synthesis*

All starting reagents were of analytical grade and used as purchased without further purification. $K_4[W(CN)_8] \cdot 2H_2O$ was prepared according to the reported methods [18]. A mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (0.0732 g, 0.2 mmol), $K_4[W(CN)_8] \cdot 2H_2O$ (0.0584 g, 0.1 mmol), 1,10-phenanthroline (0.0396 g, 0.2 mmol), and distilled water (15 mL) was sealed in a 25 mL Teflon reactor, and heated hydrothermally at 120°C for three days under autogenous pressure, and then cooled slowly to room temperature at a rate of $10°C\,h^{-1}$. The solution was filtered and the filtrate was left undisturbed at room temperature. Light-yellow single crystals suitable for X-ray structure analysis were obtained after several days. Anal. Calcd for $C_{42}H_{33}Co_2N_{12}O_{4.50}$ (%): C, 56.32; H, 3.71; N, 18.77. Found: C, 56.21; H, 3.59; N, 18.64.

Warning! Perchlorate salts are potentially explosive and should be handled in small amounts with great caution. Additionally, all preparations should be performed and stored in well-ventilated areas because cyanides are potentially poisonous compounds.

2.3. *Crystallographic data collection and structure determination*

A single crystal of dimensions ca $0.26 \times 0.22 \times 0.12$ mm was mounted on a Bruker Smart 1000 CCD diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Diffraction data were collected using the ϕ–ω scan mode at room temperature. Unit cell parameters were determined from $1.41° \leq \theta \leq 26.36°$ for the complex. An LP correction was applied to the data. Details of data collection, crystallographic data and structure refinement parameters are summarized in table 1.

The structure was solved by direct methods using SHELXS-97 [19] and refinement on F^2 was performed using SHELXL-97 by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms [20]. All hydrogen atoms

Table 1. Crystal data and details of structure determination for **1**.

Empirical formula	$C_{42}H_{33}Co_2N_{12}O_{4.50}$
Formula weight	895.66
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system and space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	
a	11.0047(16)
b	12.9587(19)
c	15.076(2)
α	100.060(2)
β	102.061(2)
γ	91.803(2)
Volume (Å^3)	2065.0(5)
Z, Calculated density (mg m^{-3})	2, 1.440
Absorption coefficient (mm^{-1})	0.862
$F(000)$	918
Crystal size (mm^3)	$0.26 \times 0.22 \times 0.12$
θ range for data collection (°)	1.41–26.36
Limiting indices	$-13 \leq h \leq 13$, $-16 \leq k \leq 13$, $-18 \leq l \leq 18$
Reflections collected/unique	11723/8313 [R(int) = 0.0237]
Completeness to $\theta = 26.36$ (%)	98.6
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.926 and 0.849
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8313/33/552
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0481$, $wR_2 = 0.1331$
R indices (all data)	$R_1 = 0.0791$, $wR_2 = 0.1527$
Largest diff. peak and hole (e Å^{-3})	0.559 and −0.494

were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of $[Co(phen)_2(CN)_2][Co(phen)(CN)_4] \cdot 4.5H_2O$ (**1**) consists of two different mononuclear complex species, one cationic unit of $[Co(phen)_2(CN)_2]^+$ (**A**), one anionic unit of $[Co(phen)(CN)_4]^-$ (**B**) and uncoordinated water molecules (lattice). The water molecules participate in O–H $\cdots$ O/N hydrogen bonding interactions to stabilize the crystal framework [21]. A perspective view of **1** with the atomic numbering schemes is presented in figure 1. Selected bond lengths and angles are given in table 2. Both in cation and anion units, each cobalt(III) center is six-coordinate and displays a distorted octahedral geometry. The Co1 centre in **A** is coordinated with two chelating phen ligands and two cyanide groups in a *cis* arrangement with the angle C1–Co1–C2 = 89.32(16)°. The dihedral angle between planes of coordinated phen ligands with the same cobalt(III) ion is ca 90.3°. The angles of the coordination sphere in complex **1** differ slightly from 90° and this distortion can be attributed to restrictions imposed by the phen ligands. The mean basal plane is constructed by the coordination of three nitrogen atoms N4, N5 and N6 from two phen ligands and one carbon atom C1 of the coordinated cyanide group. The Co1–N4, Co1–N5 and Co1–N6 distances are 1.941(3), 1.942(3) and 1.967(3) Å, respectively, and the Co1–C1 distance is 1.872(4) Å. The axial positions are occupied by N3 from one of the two phen ligand and C2 of the other coordinated cyanide group. The Co1–N3 distance is 1.975(3) Å and the Co1–C2 distance is 1.873(4) Å, respectively. The Co1–N bond distances are close to Co–N bond distances found in other Co(III) complexes with nitrogen atoms [22] and shorter than those found in Co(II) complexes [23]. The bite angles between the phen chelate rings and cobalt atom are almost the same [83.41(12)° and 83.62(12)°], and larger than that in $[Co(phen)_2(CN)_2]\cdot EtOH \cdot 2H_2O$ [24]. The Co1–C bond distances of 1.872(4) and 1.873(4) Å are in good agreement with similar Co(III)–C(cyanide) bond distances [25]. The C≡N bond distances of 1.139(5) and 1.141(5) Å are comparable to non-bridging C≡N bond distances [26]. The N1–C1–Co1 and N2–C2–Co1 bond angles at 177.4(4)°

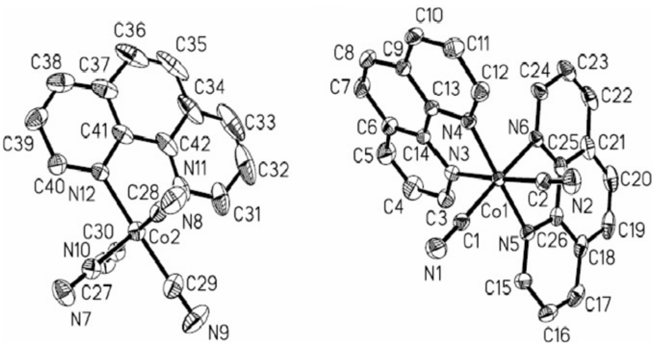

Figure 1. The ORTEP view of **1** with its H and O atoms omitted for clarity.

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

Co(1)–C(1)	1.872(4)	Co(1)–C(2)	1.873(4)
Co(1)–N(3)	1.975(3)	Co(1)–N(4)	1.942(3)
Co(1)–N(5)	1.941(3)	Co(1)–N(6)	1.967(3)
Co(2)–C(27)	1.874(4)	Co(2)–C(28)	1.902(4)
Co(2)–C(29)	1.875(5)	Co(2)–C(30)	1.906(4)
Co(2)–N(11)	1.976(4)	Co(2)–N(12)	1.974(3)
C(1)–Co(1)–C(2)	89.32(16)	C(27)–Co(2)–C(28)	88.21(18)
C(1)–Co(1)–N(3)	89.64(15)	C(27)–Co(2)–C(29)	87.7(2)
C(1)–Co(1)–N(4)	89.23(13)	C(27)–Co(2)–C(30)	90.58(17)
C(1)–Co(1)–N(5)	93.61(13)	C(27)–Co(2)–N(11)	175.91(17)
C(1)–Co(1)–N(6)	177.06(14)	C(27)–Co(2)–N(12)	94.26(15)
C(2)–Co(1)–N(3)	175.69(13)	C(28)–Co(2)–C(30)	177.49(17)
C(2)–Co(1)–N(4)	92.39(14)	C(28)–Co(2)–N(11)	88.86(17)
C(2)–Co(1)–N(5)	89.49(14)	C(28)–Co(2)–N(12)	92.17(15)
C(2)–Co(1)–N(6)	91.60(13)	C(29)–Co(2)–C(28)	88.05(18)
N(4)–Co(1)–N(3)	83.41(12)	C(29)–Co(2)–C(30)	89.70(18)
N(4)–Co(1)–N(6)	93.53(12)	C(29)–Co(2)–N(11)	95.0(2)
N(5)–Co(1)–N(3)	94.76(12)	C(29)–Co(2)–N(12)	178.02(19)
N(5)–Co(1)–N(4)	176.62(12)	C(30)–Co(2)–N(11)	92.46(16)
N(5)–Co(1)–N(6)	83.60(12)	C(30)–Co(2)–N(12)	90.11(15)
N(6)–Co(1)–N(3)	89.65(12)	N(12)–Co(2)–N(11)	83.01(16)

and 177.6(3)° indicate that the Co–C–N groups are almost linear, similar to $[Co(CN)_6]^{3-}$ [25]. The Co2 center in **B** is bonded to two N atoms from one phen ligand and four C atoms from four CN groups. For the Co2 center, the basal plane is formed by N11 and N12 of the phen ligand and the C27 and C29 of two coordinated cyanide groups, while the axial sites are occupied by C28 and C30 of the other two coordinated cyanide groups. The Co2–N11 and Co2–N12 distances at 1.976(4) and 1.974(3) Å are a little longer than their corresponding Co1–N distances. The Co–C distances involving Co2 vary from 1.874(4) to 1.906(4) Å and those Co–C equatorial bonds are shorter than the Co–C axial bonds because of different *trans* effects. The *trans* angle C28–Co2–C30 has value of 177.49(17)° and is close to linear. The C–Co–C angles with *cis* configuration involving the coordinated CN^- groups are close to 90°, and the Co–C–N angles are nearly linear. All the bond distances and angles around Co2 compare well with the corresponding values in other similar cyanide-containing cobalt(III) complexes [13b, 25].

The crystal lattice water molecules are hydrogen bonded to each other, and four CN^- groups form hydrogen-bond networks with four water molecules. The probable O–H···O and O–H···N hydrogen bonding interactions are given in table 3

Table 3. Hydrogen bond geometries in the crystal structure of **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)	Symmetry codes
O–H···O					
O1–H1B···O5	0.850	2.023	2.873	178.44	
O3–H3A···O1	0.850	1.968	2.817	178.13	
O4–H4B···O3	0.850	2.003	2.853	178.91	
O5–H5A···O2	0.850	2.391	2.813	111.20	
O–H···N					
O1–H1A···N1	0.850	2.491	3.144	134.20	
O2–H2A···N7	0.850	2.431	3.247	161.21	$-x+2, -y+1, -z$
O2–H2B···N9	0.850	2.337	2.769	111.95	
O3–H3B···N9	0.850	2.534	3.303	150.94	
O4–H4A···N8	0.850	2.264	2.840	125.09	

D = donor atom, A = acceptor atom.

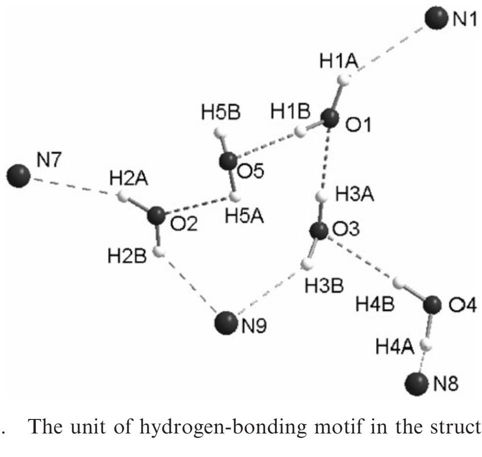

Figure 2. The unit of hydrogen-bonding motif in the structure of **1**.

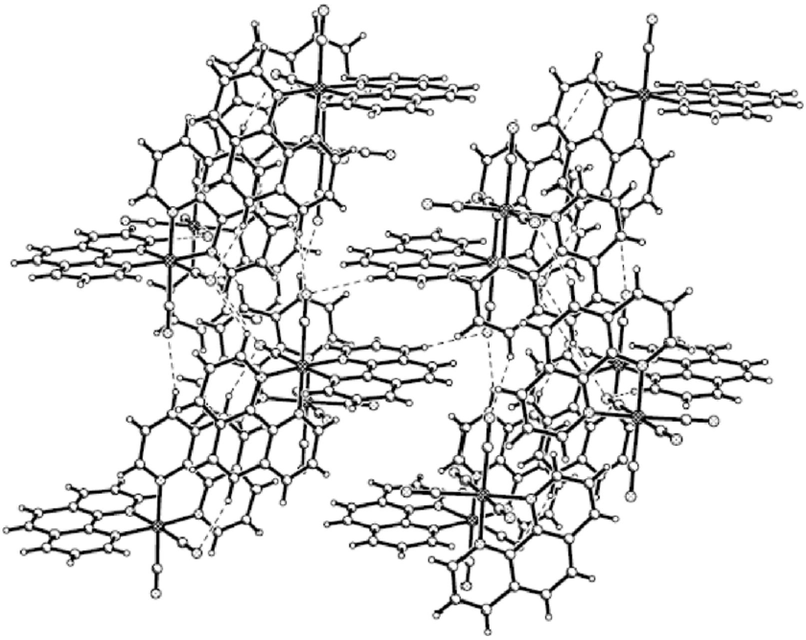

Figure 3. The perspective view of the molecule packing of **1** along the *c* axis and involving C–H···N hydrogen bonding interactions with H_2O molecules omitted for clarity.

and figure 2. Nevertheless, the N atoms of cyanide with C atoms of the phen ligands form potentially several types of weak C–H···N intermolecular hydrogen bonding interactions. The crystallographic packing diagram of **1** along the *c*-axis is shown in figure 3. Aromatic π–π stacking interactions are also apparent in **1**. Two kinds of π–π stacking interactions exist: the phenylene rings (C34 to C42) of **B** belonging to two adjacent fragments are parallel with a distance of 3.523 Å; and a plane-to-plane distance (3.647 Å) of two parallel pyridine rings (containing N4) of the adjacent **A** moieties indicate the existence of π–π stacking interactions between adjacent phen ligands [27]. In the crystal, the combination of coordinative, hydrogen bonding and π–π stacking interactions results in stabilization of a supramolecular solid-state architecture.

3.2. *Spectroscopic studies*

Infrared spectra of **1** display one sharp medium band at 2136 cm^{-1} which can be assigned to $\nu_{C\equiv N}$. The broad strong band in the range 3600–3000 cm^{-1} is attributed to the O–H stretching absorption ($\nu_{O\text{–}H}$) in H_2O molecules. The IR spectrum exhibits characteristic strong bands of the coordinated phen ligands at 1629 ($\nu_{C=C}$), 1521, 1430 ($\nu_{C=N}$), 850 ($\delta_{C\text{–}H}$ benzene ring) and 720 cm^{-1} ($\delta_{C\text{–}H}$ pyridine ring). The bands at 1521, 1430 and 720 cm^{-1} are shifted from their positions for the free phen ligands (1503, 1420 and 737 cm^{-1}), indicating nitrogen coordination [22, 24]. The appearance of a new band at 424 cm^{-1} can be assigned to ν[Co–N$_{(phen)}$].

The electronic spectra of **1** were determined in DMF solution. In the UV region, the spectra show a sharp intense band centered at 273 nm for **1** slightly blue shifted with respect to 264 nm for free phenanthroline. The corresponding band at 273 nm can be assigned to a intra-ligand (IL) π(phen)–π*(phen) band, shifted due to metal d electrons being partially delocalized over the phenanthroline. The electronic spectra of **1** also exhibit two low energy bands at ca 447 and 352 nm, which are assigned to band I ($^1A_{1g} \rightarrow {}^1T_{1g}$) and band II ($^1A_{1g} \rightarrow {}^1T_{2g}$) of the cobalt(III) d–d transitions in octahedral complexes [22a]. The inter-electronic repulsion (Racah) parameter (B_{complex}) and crystal field splitting energy ($10D_q$) are evaluated from the spectral bonds and following formula (if the usual assumption is made that $C = 4B$ [28]):

$$\nu_1 = 10D_q + 16B - C,$$
$$\nu_2 = 10D_q - C.$$

These values ($10D_q = 23{,}879\,\text{cm}^{-1}$, $B_{\text{complex}} = 377\,\text{cm}^{-1}$) indicate that a strong ligand field strong and metal-ligand bonds in the complex have an appreciable amount of covalent character ($\beta = B_{\text{complex}}/B_{\text{free ion}} < 1$) ($B_{(\text{free ion})} = 1100\,\text{cm}^{-1}$ for Co(III) [29]) [30].

Supplementary material

CCDC-287155 contains supplementary Crystallographic data (excluding structure factors) for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

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References

[1] K.R. Dunbar, R.A. Heintz. *Prog. Inorg. Chem.*, **45**, 283 (1997).

[2] S. Nishikiori, H. Yoshikawa, Y. Sano, T. Iwamoto. *Acc. Chem. Res.*, **38**, 227 (2005).

[3] W.P. Fehlhammer, M. Fritz. *Chem. Rev.*, **93**, 1243 (1993).

[4] T. Iwamoto. *J. Incl. Phenom.*, **24**, 61 (1996).

[5] J.S. Miller, J.L. Manson. *Acc. Chem. Res.*, **34**, 563 (2001).

[6] (a) D.J. Chesnut, J. Zubieta. *Chem. Commun.*, 1707 (1998); (b) D.J. Chesnut, A. Kusnetzow, J. Zubieta. *J. Chem. Soc., Dalton Trans.*, 4081 (1998); (c) D.J. Chesnut, D. Hagrman, P.J. Zapf, R.P. Hammond, R. LaDuca, R.C. Haushalter, J. Zubieta. *Coord. Chem. Rev.*, **190**, 757 (1999) and references cited therein; (d) D.J. Chesnut, A. Kusnetzow, R.R. Birge, J. Zubieta. *Inorg. Chem.*, **38**, 2663 (1999); (e) D.J. Chesnut, A. Kusnetzow, R. Birge, J. Zubieta. *Inorg. Chem.*, **38**, 5484 (1999); (f) D.J. Chesnut, D. Plewak, J. Zubieta. *J. Chem. Soc., Dalton Trans.*, 2567 (2001); (g) D.J. Chesnut, A. Kusnetzow, R. Brige, J.A. Zubieta. *J. Chem. Soc., Dalton Trans.*, 2581 (2001).

[7] N.S. Persky, J.M. Chow, K.A. Poschmann, N.N. Lacuesta, S.L. Stoll. *Inorg. Chem.*, **40**, 29 (2001).

[8] (a) A.M. Chippindale, S.J. Hibble, A.R. Cowley. *Inorg. Chem.*, **43**, 8040 (2004); (b) S.J. Hibble, A.M. Chippindale. *Z. Anorg. Allg. Chem.*, **631**, 542 (2005).

[9] (a) T. Pretsch, I. Brüdgam, H. Hartl. *Z. Anorg. Allg. Chem.*, **630**, 353 (2004); (b) T. Pretsch, H. Hartl. *Z. Anorg. Allg. Chem.*, **630**, 1581 (2004).

[10] D.Q. Chu, L.M. Wang, J.Q. Xu. *Mend. Commun.*, **1**, 25 (2004).
[11] J.-D. Lin, Z.-H. Li, T. Li, J.-R. Li, S.-W. Du. *Inorg. Chem. Commun.*, **9**, 675 (2006).
[12] B. Yan, V.O. Golub, A. Lachgar. *Inorg. Chim. Acta*, **359**, 118 (2006).
[13] (a) E. Colacio, J.M. Domínguez-Vera, F. Lloret, J.M. Moreno-Sánchez, R. Kivekäs, A. Rodríguez, R. Sillanpää. *Inorg. Chem.*, **42**, 4209 (2003); (b) A. Rodriguez, H. Sakiyama, N. Masciocchi, S. Galli, N. Gálvez, F. Lloret, E. Colacio. *Inorg. Chem.*, **44**, 8399 (2005); (c) E. Colacio, A. Debdoubi, R. Kivekäs, A. Rodríguez. *Eur. J. Inorg. Chem.*, 2860 (2005).
[14] J.-H. Yu, J.-Q. Xu, Q.-X. Yang, L.-Y. Pan, T.-G. Wang, C.-H. Lü, T.-H. Ma. *J. Mol. Struct.*, **658**, 1 (2003).
[15] X. He, C.-Z. Lu, D.-Q. Yuan, S.-M. Chen, J.-T. Chen. *Eur. J. Inorg. Chem.*, 2181 (2005).
[16] H. Mao, C. Zhang, C. Xu, H. Zhang, X. Shen, B. Wu, Y. Zhu, Q. Wu, H. Wang. *Inorg. Chim. Acta*, **358**, 1934 (2005).
[17] X.-B. Chen, Y.-Z. Li, X.-Z. You. *Appl. Organometal. Chem.*, **20**, 305 (2006).
[18] L.D. Bok, J.G. Leipoldt, S.S. Basson. *Z. Anorg. Allg. Chem.*, **415**, 81 (1975).
[19] G.M. Sheldrick. *SHELXS-97. Program for the Solution of Crystal Structure*, University of Göttingen, Germany (1997).
[20] G.M. Sheldrick. *SHELXS-97. Program for the Refinement of Crystal Structure*, University of Göttingen, Germany (1997).
[21] C.R. Choudhury, S.K. Dey, S. Mitra, N. Mondal, J. Ribas, K.M.A. Malik. *Bull. Chem. Soc. Jpn.*, **77**, 959 (2004).
[22] (a) B.-H. Ye, T.-X. Zeng, P. Han, L.-N. Ji. *Trans. Met. Chem.*, **18**, 515 (1993); (b) B.-H. Ye, X.-M. Chen, T.-X. Zeng, L.-N. Ji. *Polyhedron*, **13**, 2185 (1994).
[23] (a) J. Faus, M. Julve, F. Lloret, J.A. Real, J. Sletten. *Inorg. Chem.*, **33**, 5535 (1994); (b) M. Yuan, Y. Li, E. Wang, Y. Lu, C. Hu, N. Hu, H. Jia. *J. Chem. Soc., Dalton Trans.*, 2916 (2002).
[24] F. Jian, H. Xiao, L. Li, P. Sun. *J. Coord. Chem.*, **57**, 1131 (2004).
[25] (a) V. Marvaud, C. Decroix, A. Scuiller, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer. *Chem. Eur. J.*, **9**, 1678 (2003); (b) V. Marvaud, C. Decroix, A. Scuiller, F Tuyèras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer. *Chem. Eur. J.*, **9**, 1692 (2003).
[26] N. Mondal, D.K. Day, S. Mitra, V. Gramlich. *Polyhedron*, **20**, 607 (2001).
[27] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[28] J.S. Griffith. *The Theory of Transition-Metal Ions*, Cambridge University Press, New York (1961).
[29] H.L. Schläfer, G. Gliemann. *Basic Principles of Ligand Field Theory*, Wiley-Interscience, London (1969).
[30] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam (1997).