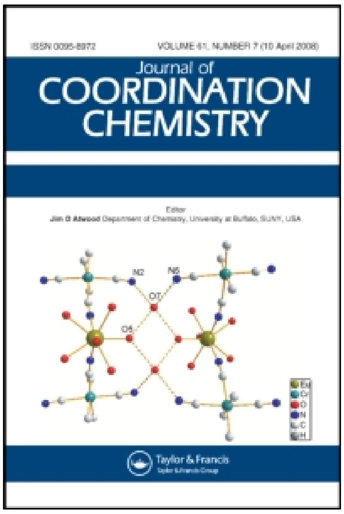

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, Structures and Characterization of Cobalt(II) and Cobalt(III) Complexes with *N*-Benzylated Polyamines and a Terminal Azido Ligand

Hui Jiang[ab]; Yong-Shu Xie[ab]; Zhong-Yuan Zhou[c]; Xiao-Long Xu[b]; Qing-Liang Liu[b]
[a] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, P.R. China [b] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, P.R. China [c] Department of Applied Biology and Chemical Technology, The Hongkong Polytechnic University, Kowloon, Hongkong P.R. China

To cite this Article Jiang, Hui , Xie, Yong-Shu , Zhou, Zhong-Yuan , Xu, Xiao-Long and Liu, Qing-Liang(2003) 'Syntheses, Structures and Characterization of Cobalt(II) and Cobalt(III) Complexes with *N*-Benzylated Polyamines and a Terminal Azido Ligand', Journal of Coordination Chemistry, 56: 9, 825 — 832

To link to this Article: DOI: 10.1080/0095897031000123804

URL: http://dx.doi.org/10.1080/0095897031000123804

J. Coord. Chem., Vol. 56, No. 9, 15 June 2003, pp. 825–832

SYNTHESES, STRUCTURES AND CHARACTERIZATION OF COBALT(II) AND COBALT(III) COMPLEXES WITH *N*-BENZYLATED POLYAMINES AND A TERMINAL AZIDO LIGAND

HUI JIANG[a,b], YONG-SHU XIE[a,b], ZHONG-YUAN ZHOU[c], XIAO-LONG XU[b] AND QING-LIANG LIU[b,]*

[a]*Department of Chemistry,* [b]*State Key Laboratory of Fire Science,*
University of Science and Technology of China, Hefei, Anhui, 230026, P.R. China;
[c]*Department of Applied Biology and Chemical Technology, The Hongkong*
Polytechnic University, Hung Hom, Kowloon, Hongkong, P.R. China

(Received 11 September 2002; Revised 11 December 2002; In final form 3 April 2003)

Mononuclear cobalt(II) and cobalt(III) complexes, [Co(trenb)(N_3)]Cl (**1**) and [Co(dienb)(N_3)$_2$(OAc)] (**2**) (trenb = tris[2-(benzylamino)ethyl]amine, dienb = 1,9-diphenyl-2,5,8-triazanonane) were synthesized and characterized by elemental analyses, IR and electronic spectra. Their crystal structures were also determined by X-ray diffraction analyses. In Complex **1**, cobalt(II) is five-coordinate trigonal bipyramidal with one azido nitrogen atom and four nitrogen donors of the tripodal ligand; the chloride interacts weakly with one of the secondary amino groups of trenb via a hydrogen bond. In Complex **2**, cobalt(III) is in a distorted octahedral coordination environment, consisting of three nitrogen atoms of the amine ligand, two azide nitrogen atoms and an oxygen atom of the acetate ion; a six-membered ring involving the hydrogen bond may stabilize the complex, which maintains its solid geometry in DMF as indicated by the electronic spectrum.

Keywords: Crystal structures; Cobalt complexes; Polyamine complexes; Azido ligand

INTRODUCTION

Linear polyamines are of great interest from several perspectives. Their binding properties, which are widely utilized in biological system, have been extensively studied [1]. Polyamine complexes also attract much attention, including those of Co(II) [2] and Co(III) [3]. *N*-Alkylation of the polyamines is known to inhibit the coordinating ability of the primary amine as a result of an increase in steric hindrance, and influences their original coordinating modes [4]. Among the modifications, there have been few reports

---

*Corresponding author. Fax: +86 551 360 3388. E-mail: qliu@ustc.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000123804

concerning *N*-benzylation [5,6b] and information about their complexes is relatively scarce [6]. Herein, we report the preparation of two *N*-benzylated polyamines: tris[2-(benzylamino)ethyl]amine (trenb) and 1,9-diphenyl-2,5,8-triazanonane (dienb).

The participation of azide groups often induces various kinds of change in the structure and properties, especially in magnetism [7], which have attracted considerable attention [6a].

We have synthesized and characterized two azido-polyamine-cobalt complexes, i.e., [Co(trenb)(N_3)]Cl (**1**) and [Co(dienb)(N_3)$_2$(OAc)] (**2**). X-ray analyses reveal that the coordination geometries are distorted trigonal bipyramidal for Co(II) and octahedral for Co(III), respectively.

EXPERIMENTAL

Reagents and Apparatus

Tren (tris(2-aminoethyl)amine), benzaldehyde and dien (1,4,7-triazaheptane) was purchased from Fluka. All other reagents were AR grade from Shanghai Chemical Reagent Company.

^{1}H NMR spectra were recorded on a Bruker DMX-500 spectrometer in d_6-DMSO solution at 298 K and chemical shifts (δ, ppm) are given relative to internal tetramethylsilane. IR spectra were recorded on a Bruker Vector-22 spectrometer (KBr disc). Electronic spectra were obtained on a Shimadzu UV-3100 UV-Vis-NIR recording spectrophotometer (λ_{max} in nm, ε in $M^{-1}\,cm^{-1}$) in the range 200–900 nm. Microanalyses of C, H and N were carried out with a VARIO ELIII elemental analyzer.

Caution! Azido salts are potentially explosive. Only a small amount of the material should be prepared and it should be handled with extreme care.

Syntheses of Compounds

Polyamine Ligand

The ligand dienb · 3HCl was synthesized according to a modified literature method by reaction of benzaldehyde with 1,4,7-triazaheptane followed by reaction with excess KBH_4 [5]. The final product was precipitated under acidic condition. Yield 63%. Anal. Calcd. for $C_{18}H_{28}N_3Cl_3$ (%): C, 55.04; H, 7.18; N, 10.70. Found: C, 54.95; H, 7.03; N, 10.85. IR (KBr, cm^{-1}): 2982 (s), 2936 (m), 2500 ~ 2800 (br), 1585 (m), 1480 (m), 1454 (s), 1047 (s), 814 (s), 744 (s), 698 (s), 600 (s), 512 (s). ^{1}H NMR, δ(d_6-DMSO): 7.16–7.45 (s, 10 H, aryl), 4.22 (s, 4 H, ArCH_2–), 3.42 (s, 8 H, –NH_2^+CH_2). Trenb · 3HCl was obtained similarly, starting from tris(2-aminoethyl)amine and benzaldehyde. Yield 55%. IR (KBr, cm^{-1}): 2927 (m), 2500 ~ 2800 (br), 1587 (m), 1456 (s), 1435 (m), 1371 (m), 1216 (w), 1022 (m), 925 (m), 861 (w), 744 (s), 694 (s). Anal. Calcd. for $C_{27}H_{39}Cl_3N_4$ (%): C, 61.65; H, 7.47; N, 10.65. Found: C, 61.43; H, 7.45; N, 10.72. ^{1}H NMR, δ(d_6-DMSO): 7.42–7.65 (s, 15H, aryl), 4.22 (s, 6H, ArCH_2–), 3.12 (s, 6H, Ar$CH_2NH_2^+$CH_2–), 2.80 (s, 6H, > NCH_2–).

Preparation of [Co(trenb)(N_3)]Cl (1)

Co(OAc)$_2$(4H$_2$O (0.050 g, 0.20 mmol), trenb · 3HCl (0.105 g, 0.20 mmol), NaOH (4.0 M, 0.15 mL, 0.60 mmol) were added to 50 mL methanol successively and the solution became dark blue. A solution of NaN$_3$ (0.026 g, 0.40 mmol) in a small quantity of water was then added and a grass-green solution was obtained. The solution was refluxed for 3 h, and concentrated in vacuo. Green crystals suitable for X-ray diffraction were collected several days later, washed with ether and dried. Yield: 0.035 g, 16%. IR (KBr, cm^{-1}): 3155 (m, NH), 2056 (s, N$_3$–), 1454 (m), 1007 (m), 744 (m), 704 (s). Anal. Calcd. for $C_{27}H_{36}ClCoN_7$ (%): C, 58.64; H, 6.56; N, 17.73. Found: C, 58.31; H, 6.55; N, 17.36.

Preparation of [Co(dienb)(N_3)$_2$(OAc)] (2)

The dienb · 3HCl (0.157 g, 0.40 mmol) was dissolved in methanol (50 mL). Co(OAc)$_2$(4H$_2$O (0.100 g, 0.40 mmol) was then added and a dark red solution formed. Several drops of H_2O_2 were added slowly and the color immediately darkened. NaN$_3$ (0.052 g, 0.80 mmol) in a small amount of water was added to the solution, refluxed for 3 h, then concentrated in vacuo. The resulting dark brown powder was collected, washed with ether and dried. Yield: 0.047 g, 24%. IR (KBr, cm^{-1}): 3192 (m, NH), 2926 (w), 2058 and 2030 (s, N$_3$–), 1586 (s), 1453 (m), 1376 (m), 1003 (m), 757 (s), 702 (s). Anal. Calcd. for $C_{20}H_{28}CoN_9O_2$ (%): C, 49.49; H, 5.81; N, 25.97. Found: C, 49.65; H, 5.67; N, 26.38. Crystals suitable for X-ray analysis were grown by slow evaporation of a methanol solution of the complex.

Crystal Structure Determination

The crystals were mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo Kα radiation. The data were collected at a temperature of 20 ± 1°C and corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters. All calculations were performed using the SHELXTL-97 software package [8]. The crystal data, data collection and structure refinement are summarized in Table I.

RESULTS AND DISCUSSION

Crystal Structures

A perspective drawing for Complex **1** is shown in Fig. 1 and selected bond lengths and angles are listed in Table II. The cobalt(II) in Complex **1** is five-coordinate with one azide nitrogen atom and four nitrogen donors of the tripodal ligand. Its geometry, the distorted trigonal bipyramid, is quite common for cobalt(II) complexes. The pseudo-three-fold axis is aligned with N(1)–Co–N(5) [175.99 (13)°] and the equatorial plane containing three secondary amino nitrogen atoms is close to an equilateral

TABLE I Crystal data and processing parameters for Complex **1** and **2**

Compound	**1**	**2**
Molecular formula	$C_{27}H_{36}ClCoN_7$	$C_{20}H_{28}CoN_9O_2$
Formula weight	553.01	485.44
Crystal color and habit	blue, prism	dark red, plate
Crystal dimension (mm)	0.14 × 0.10 × 0.10	0.20 × 0.18 × 0.12
System space group	orthorhombic, pbca	monoclinic, p2(1)/c
a (Å)	14.463(2)	11.6356(17)
b (Å)	15.399(2)	22.059(3)
c (Å)	25.372(4)	9.8138(14)
β (°)	90	113.395(3)
V (Å^3)	5650.6(15)	2311.8(6)
Z	8	4
D_c (kg/m^3)	1.300	1.395
μ(Mo Kα), mm^{-1}	0.730	0.778
F(000)	2328	1016
θ range (°)	1.0–27.5	1.0–27.5
hkl range	−12/14, −37/36, −12/12	−12/15, −28/27, −12/12
Measured refl. number	35467	15099
Independent refl. number	6484	5314
Observed refl. ($I \geq 2\sigma(I)$)	1466	1660
R^a	0.0595	0.0585
$R_w{}^b$	0.1124	0.1425
GOF^c	0.676	0.724
Data/restraint/parameters	6484/11/325	5314/0/288
Residual electron density, e Å^{-3}	0.515/−0.512	0.910/−0.337

[a] $R(F)=\sum||F_0|-|F_c||/\sum|F_0|$; [b] $wR(F^2)=[\sum(w(F_0^2-F_c^2))^2/(\sum w(F_0^2))^2]^{1/2}$; [c] $\mathrm{GOF}=[\sum(w(F_0^2-F_c^2)^2)/(N_{\mathrm{diffrs}}-N_{\mathrm{params}})]^{1/2}$.

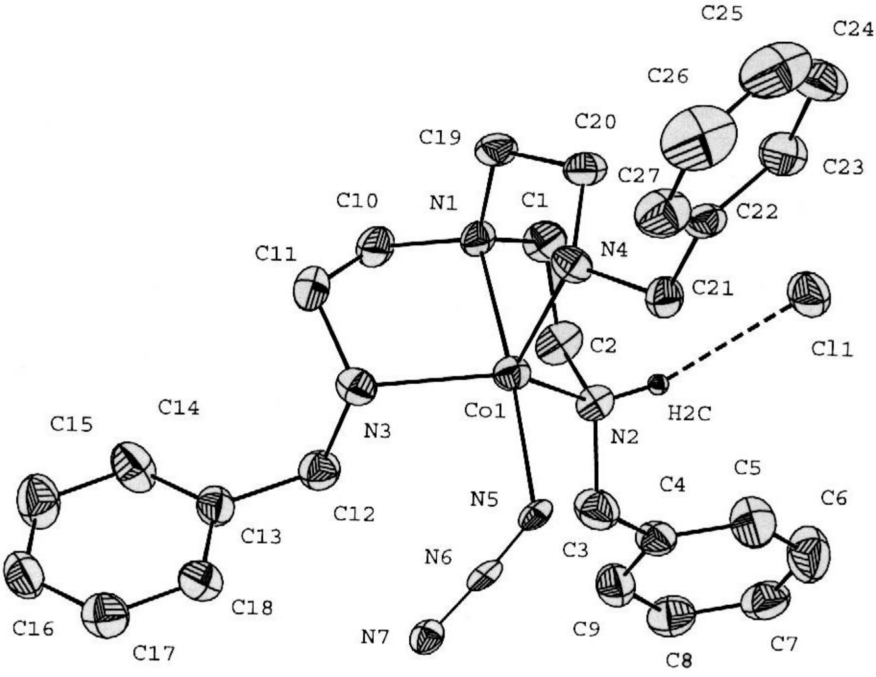

FIGURE 1 Molecular structure of [Co(trenb)(N$_3$)]Cl (**1**). The scheme (30% probability) shows the weak interaction N–H···Cl.

TABLE II Selected bond lengths (Å) and bond angles (°) for **1**

Co(1)–N(5)	2.220(3)	Co(1)–N(3)	2.095(4)
Co(1)–N(2)	2.092(4)	Co(1)–N(1)	2.227(3)
Co(1)–N(4)	2.087(3)	N(6)–N(7)	1.151(5)
N(5)–N(6)	1.133(4)		
N(5)–Co(1)–N(2)	100.80(13)	N(5)–Co(1)–N(3)	95.47(14)
N(2)–Co(1)–N(3)	119.17(14)	N(5)–Co(1)–N(4)	102.11(13)
N(2)–Co(1)–N(4)	115.24(14)	N(3)–Co(1)–N(4)	117.70(14)
N(5)–Co(1)–N(1)	175.99(13)	N(2)–Co(1)–N(1)	80.89(14)
N(3)–Co(1)–N(1)	80.55(14)	N(4)–Co(1)–N(1)	80.28(13)
N(6)–N(5)–Co(1)	135.5(4)	N(5)–N(6)–N(7)	173.1(11)

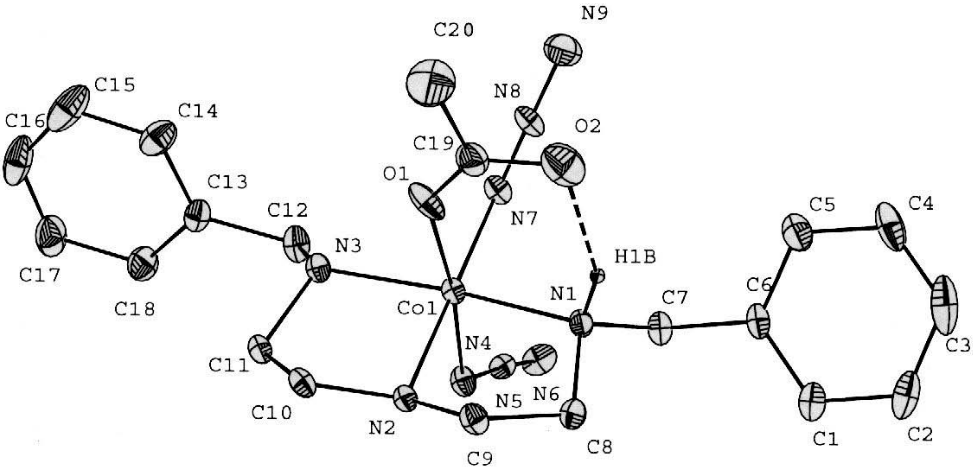

FIGURE 2 View of [Co(dienb)$(N_3)_2$(OAc)] (**2**) (10% probability). The hydrogen bond between N(1)–H(1B)$\cdots$O(2) leads to the formation of a six-membered ring.

triangle. The cobalt(II) ion is about 0.34 Å out of the plane towards the N_3^-. The Co–$N_{\text{tertiary amine}}$ distance [2.227(3) Å] is significantly longer than the other three nitrogen atoms from trenb (range from 2.087(3) to 2.095(4) Å) and similar to those reported [9,10]. However, the Co–N_{azido} distance [2.220(3) Å] almost equals that of the Co–$N_{\text{tertiary amine}}$ and is much longer than that reported in the literature [9]. Also note that the Cl(1)$\cdots$H(2C)–N(2) distance (2.403 Å) is rather short, indicating that the chloride plays the role of charge balance, and also interacts weakly with one secondary amine of the trenb ligand via hydrogen bonds.

The molecular structure of Complex **2** is shown in Fig. 2. Selected bond lengths and bond angles are given in Table III. The cobalt(III) is in a distorted octahedral environment with three nitrogen atoms from dienb, two azide nitrogen atoms and an oxygen atom of the acetate ion. The three nitrogen donors of the polyamine ligand form a mer- geometry and the two terminal azido ligands coordinate at *cis*-positions. The most strained angle is N(1)–Co–N(3), which is 9.2° deviated from the ideal value for a *trans* pair, and the two Co–N_{amine} bonds are the longest [11], which may be induced by steric hindrance of the benzylic groups. In the equatorial plane, the two Co–N_{azido} bonds are almost isometric. The acetate ion is monodentate. The bond length of

TABLE III Selected bond lengths (Å) and bond angles (°) for **2**

Co(1)–N(7)	1.941(3)	Co(1)–N(2)	1.938(3)
Co(1)–N(3)	1.990(3)	Co(1)–N(4)	1.943(3)
Co(1)–N(1)	1.972(3)	Co(1)–O(1)	1.955(3)
O(1)–C(19)	1.117(5)	O(2)–C(19)	1.268(6)
N(4)–N(5)	1.180(4)	N(5)–N(6)	1.145(4)
N(7)–N(8)	1.142(4)	N(8)–N(9)	1.145(5)
N(2)–Co(1)–N(7)	176.94(12)	N(2)–Co(1)–N(4)	85.01(12)
N(7)–Co(1)–N(4)	92.11(13)	N(2)–Co(1)–O(1)	90.47(11)
N(7)–Co(1)–O(1)	92.31(12)	N(4)–Co(1)–O(1)	173.18(13)
N(2)–Co(1)–N(1)	86.35(11)	N(7)–Co(1)–N(1)	94.80(12)
N(4)–Co(1)–N(1)	92.41(11)	O(1)–Co(1)–N(1)	92.39(11)
N(2)–Co(1)–N(3)	85.47(11)	N(7)–Co(1)–N(3)	93.58(12)
N(4)–Co(1)–N(3)	91.02(11)	O(1)–Co(1)–N(3)	83.52(12)
N(1)–Co(1)–N(3)	170.82(12)	C(19)–O(1)–Co(1)	135.4(3)
N(5)–N(4)–Co(1)	124.4(3)	N(6)–N(5)–N(4)	174.9(4)
N(8)–N(7)–Co(1)	122.1(3)	N(7)–N(8)–N(9)	174.7(4)

C=O(2) was measured to be 1.268(6) Å, a little longer than the normal C=O bond length (about 1.20 Å), from the influence of the hydrogen bond between N(1)–H(1B)···O(2) (1.987 Å, 152.17°). Also the hydrogen bond strains the angle, N(1)–Co–N(3). The complex may be stabilized by a six-membered ring involving the hydrogen bond and the cobalt(III) ion, as shown by the fact that the bond length of Co–N(1) is about 0.02 Å shorter than that of Co–N(3).

IR Spectra

The IR spectrum of **1** shows the $\nu_{asym}(N_3)$ stretching vibration as a sharp band at 2056 cm^{-1}, consistent with the presence of terminally bonded azide. The relevant bands of Complex **2** at 2030 and 2058 cm^{-1} are consistent with the *cis*-configuration between the azido ligands, as Massoud *et al.* [12] have concluded. The *cis*-diazido species exhibit two strong absorption bands in the range 2000–2065 cm^{-1}, whereas the corresponding *trans*-complex shows only one band in the region. The bands near 3200 cm^{-1} were assigned to the stretching modes of the coordinated NH groups, which disappeared in the "free" ligand from protonation of the amines. In Complex **2** the asymmetric carboxylate stretch ν_{as} appears at 1586 cm^{-1}, accompanied with the symmetric vibration ν_s at 1377 cm^{-1}. The 209 cm^{-1} between ν_{as} and ν_s suggests that acetate acts as a monodentate ligand [13], in accord with the crystal structure.

Electronic Spectra

Electronic spectral data are collected in Table IV. The electronic spectrum of Complex **1** in DMF shows two broad *d–d* bands of close intensities at 608 and 489 nm, with a shoulder at lower energy (754 nm), indicative of a distorted trigonal bipyramidal geometry around the cobalt(II) atom [14]. Remaining bands near or below 300 nm are due to ligand internal transitions, based on the similarities with the absorbance of the "free" ligand. The spectrum of Complex **2** was measured in both DMF and dichloromethane. The *d–d* transition appears at 558 nm in DMF and slightly (5 nm) blue shifted from that in dichloromethane solution, consistent with the spin-allowed *d–d* transition $^1A_{1g} \rightarrow ^1T_{2g}$ [10,14], indicating that the complex maintains its pseudo-octahedral coordination geometry in DMF solution.

TABLE IV Summary of electronic spectra data

Complex	*Solvent*	λ_{max}/nm (ε/M^{-1} cm^{-1})
1	DMF	754 (26), 608 (109), 489 (107), 316 (553), 266 (622)
2	DMF	558 (417), 314 (16 700), 264 (12 100)
	CH_2Cl_2	563 (438), 308 (18 600), 234 (16 300)

SUMMARY

The crystal structures of mononuclear cobalt(II) and cobalt(III) complexes with *N*-alkylated polyamine and azido groups have been determined by X-ray diffraction analyses. The chloride in the cobalt(II) complex interacts weakly with one secondary amine via a hydrogen bond, and the six-membered ring involving the hydrogen bond in the cobalt(III) complex may stabilize the structure.

The two complexes can be utilized as multi-dimensional building blocks for novel supramolecules, since the azido ligand in the complexes are both coordinated terminally and retain their coordinating ability. Thus, the work proposed in the next step is to study the self-assembly of these potential materials.

Acknowledgement

The project is supported by the National Science Foundation of Anhui Province (No. 01045408).

Supplementary Material

A full list of crystallographic data is available from the authors upon request.

References

[1] (a) M.L. Edwards, R.D. Snyder and D.M. Stemerick, *J. Med. Chem.* **34**, 2414 (1991); (b) P. Scrimin, P. Tecilla, U. Tonellato, G. Valle and A. Veronese, *Chem. Commun.* 1163 (1995).

[2] See Examples: (a) N. Ceccanti, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, R. Pardini, R. Pontellini and M.R. Tine, *Inorg. Chim. Acta.* **321**, 153 (2001); (b) D.A. House, J. Browning, L. Zipper and W. Marty, *Inorg. Chim. Acta.* **288**, 181 (1999).

[3] See Examples: (a) A. Derwahl, A.J. Dickie and D.A. House, *Inorg. Chim. Acta.* **257**, 179 (1997); (b) R.L. Fanshawe, A. Mobinikhaledi, C.R. Clark and A.G. Blackman, *Inorg. Chim. Acta.* **307**, 26 (2000); (c) J.M. Harrowfield, Y. Kim, M. Mocerino, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.* 2431 (1995).

[4] (a) X. Zhang, J.L. Wang, M. Yu and F.M. Miao, *Acta Chimica Sinica* **58**, 1280 (2000); (b) B. Kwak, K.W. Cho, M. Pyo and M.S. Lah, *Inorg. Chim. Acta.* **290**, 21 (1999); (c) A.R. Oki, P. Gogineni, M. Yurchenko and V.G. Young, *Inorg. Chim. Acta.* **257**, 279 (1997); (d) M.S. Lah and M. Moon, *Bull. Kor. Chem. Soc.* **18**, 406 (1997); (e) J.W. Lim, M. Mikuriya and H. Sakiyama, *Bull. Chem. Soc. Jpn.* **74**, 2131 (2001).

[5] (a) J.A. Sclafani, M.T. Maranto, T.M. Sisk and S.A. Van Arman, *J. Org. Chem.* **61**, 3221 (1996); (b) F. Felluga, P. Tecilla, L. Hillier, C.A. Hunter, G. Licini and P. Scrimin, *Chem. Commun.* 1087 (2000).

[6] (a) Y.S. Xie, Q.L. Liu, H. Jiang, C.X. Du, X.L. Xu, M.G. Yu and Y. Zhu, *New J. Chem.* **26**, 176 (2002); (b) M.A. Bernardo, F. Pina, E. Garcia-Espana, J. Latorre, S.V. Luis, J.M. Llinares, J.A. Ramirez and C. Soriano, *Inorg. Chem.* **37**, 3935 (1998).

[7] Examples include: (a) O. Kahn, *Molecular Magnetism* (VCH, Weinheim, 1993); (b) M.A.S. Goher, J. Cano, Y.M. Journaux, A.M. Abu-Youssef, F.A. Mautner, A. Escuer and R. Vicente, *Chem.-Eur. J.* **6**, 778 (2000); (c) P.S. Mukherjee, T.K. Maji, G. Mostafa, W. Hibbs and N.R. Chaudhuri, *New J. Chem.* **25**, 760 (2001).

[8] G.M. Sheldrick, SHELXTL97. Program for Crystal Structure Refinement (University of Göttigen, Germany, 1997).

[9] (a) Z.H. Zhang, H.L. Yang, Z.H. Ma and A.D. Qi, *Chinese J. Chem.* **18**, 842 (2000); (b) M.A.S. Goher and F.A. Mautner, *Polyhedron*, **18**, 2339 (1999).

[10] S. Bhattacharyya, D. Ghosh, S. Mukhopadhyay, W.P. Jensen, E.R.T. Tiekink and M. Chaudhury, *J. Chem. Soc., Dalton Trans.* 4677 (2000).

[11] D.C. Ware, P.J. Brothers, G.R. Clark, W.A. Denny, B.D. Palmer and W.R. Wilson, *J. Chem. Soc., Dalton Trans.* 925 (2000).

[12] (a) S.S. Massoud, F.A. Mautner, M. Abu-Youssef and N.M. Shuaib, *Polyhedron*, **18**, 2287 (1999); (b) S.S. Massoud, *Polyhedron* **13**, 3127 (1994).

[13] (a) C.K. Sams, F. Somoza, I. Bernal and H. Toftlund, *Inorg. Chim. Acta* **318**, 45 (2001); (b) J. Springborg and H. Toftlund, *Acta Chem. Scand., Ser. A* **33**, 31 (1979); (c) G.B. Deacon and R.J. Philips, *J. Coord. Chem. Rev.* **33**, 227 (1980).

[14] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Edn. (Elsevier, Amsterdam, 1984), p. 492.