Polish J. Chem., **78**, 761–769 (2004)

Antiferromagnetically Coupled Chromium(III)–Chromium(III) Binuclear Complexes with Tris(oxalato)chromate(III)

by Y.-T. Li[1*], J.-F. Lou[1] and C.-W. Yan[2]

[1]*Marine Drug & Food Institute, Ocean University of China, 5 Yushan Road, Qingdao, Shandong, 266003, P. R. China*
[2]*College of Marine Life Sciences, Ocean University of China, Qingdao, 266003, P. R. China*

(Received January 29th, 2004)

Three new binuclear chromium(III) complexes bridged by tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$ and end-capped with 2,2′-bipyridine (bpy); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 5-methyl-1,10-phenanthroline (Mephen), have been synthesized and characterized, namely $[Cr_2(ox)_3(bpy)_2]$ **(1)**, $[Cr_2(ox)_3(Me_2bpy)_2]$ **(2)** and $[Cr_2(ox)_3(Mephen)_2]$ **(3)**. At present, the three complexes have not yet been isolated in crystalline form, suitable for X-ray structure analysis, but based on elemental analyses, molar conductance and magnetic moments of room-temperature measurements, and spectroscopic studies, extended ox-bridged structures consisting of two chromium(III) ions, each in an octahedral environment are proposed for these complexes. The complexes $[Cr_2(ox)_3(bpy)_2]$ **(1)** and $[Cr_2(ox)_3(Me_2bpy)_2]$ **(2)** were further characterized by variable temperature magnetic susceptibility (4.2~300 K) measurements and the observed data were successfully simulated by the equation based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, giving the exchange integrals $J = -9.73$ cm^{-1} for **(1)** and $J = -5.29$ cm^{-1} for **(2)**. This result indicates the presence of weak antiferromagnetic spin-exchange interaction between the metal ions within each molecule. The influence of the methyl substituents in the terminal ligand on magnetic interactions between the metals is also discussed.

Key words: μ-oxalato-bridge, binuclear chromium(III) complexes, antiferromagnetic interaction, synthesis

The synthesis and magnetic investigations of exchange-coupled transition metal complexes, in which the spin coupling between the paramagnetic metals is propagated by multiatom bridges, have been an active field of research with the aim of understanding fundamental factors, governing the magnetic properties of transition-metal complexes and to obtain some useful information about designing molecule-based magnets and to mimic the active sites and function of biological substances [1–10].

Owing to their fundamental importance in the magnetic studies, much effort has been devoted to the development of multiatom bridging ligands, that can afford magnetic interactions. Among other more elaborate ligands employed in the study of magnetic interactions, the oxalato group, due to both its versatile bonding mode with

*Author to whom all correspondence should be addressed. E-mail: yantuanli@163.com

metal ions and its remarkable ability to transmit electronic effects, when acting as bridges between paramagnetic centers, has been shown to be an excellent multiatom bridging ligand in supporting magnetic exchange interactions. Several kinds of polynuclear complexes, bridged by the oxalato groups, have been synthesized and their magnetic properties studied [11–15]. However, to the best of our knowledge, no oxalato-bridged chromium(III)–chromium(III) binuclear complexes have so far been reported. Taking into account the above facts, it is of considerable interest to synthesize and study chromium(III)–chromium(III) binuclear complexes with bridging oxalato, in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper, three new μ-oxalato-bridged binuclear chromium(III) complexes, which have the general formula $[Cr_2(ox)_3(L)_2]$ (ox = oxalato dianions, L = bpy, Me_2bpy, Mephen), have been synthesized and characterized by using tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$, as polyatomic bridging ligand. The cryomagnetic properties of the $[Cr_2(ox)_3(bpy)_2]$ **(1)** and $[Cr_2(ox)_3(Me_2bpy)_2]$ **(2)** complexes were measured and studied in the temperature range 4.2~300 K. At present, the three binuclear complexes have not been obtained in crystalline form, suitable for X-ray structure analysis. However, the combination of magnetic susceptibility and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of the binuclear complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Potassium tris(oxalato)chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$) and $Cr(ClO_4)_3\cdot 6H_2O$ were synthesized according to the literature methods [16,17]. The terminal ligands 2,2′-bipyridine (bpy); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 5-methyl-1,10-phenanthroline (Mephen), were used as commercially obtained.

Synthesis of $[Cr_2(ox)_3(bpy)_2]$ (1): A methanol solution (10 mL) of $K_3[Cr(ox)_3]\cdot 3H_2O$ (1.0 mmol, 491 mg) was added successively dropwise to a solution of $Cr(ClO_4)_3\cdot 6H_2O$ (1.1 mmol, 504 mg) stirred in methanol (15 mL). The vigorous stirring was continued at room temperature until the mixture became limpid (about 10 minutes). It was then filtered to eliminate impurities. A methanol solution (15 mL) of bpy (2.0 mmol, 312 mg) was added to the filtrate. The solution changed colour immediately and a small amount of brown precipitate was formed. After stirring the mixture for *ca.* 8 h the brown microcrystals, thus formed were filtered, washed with methanol, water and diethyl ether several times and dried over P_2O_5 under reduced pressure. It was recrystallized from an acetonitrile solution and the brown needle crystals were obtained. Yield, 422 mg (62%), m.p. 288.7°C. Anal. Calc. for $Cr_2C_{26}H_{16}N_4O_{12}$ (m.w. 680.42): C, 45.90; H, 2.37; N, 8.23; Cr, 15.28%. Found: C, 45.72; H, 2.13; N, 8.01; Cr, 15.16%.

Synthesis of $[Cr_2(ox)_3(Me_2bpy)_2]$ (2): This complex was obtained as red-brown microcrystals by the same procedure as above but by using Me_2bpy (368 mg, 2 mmol) instead of bpy. It was recrystallized from a DMF/ethanol (1:3) mixture and the needle crystals were collected. Yield, 552 mg (75%), m.p. 301.3°C. Anal. Calc. for $Cr_2C_{30}H_{24}N_4O_{12}$ (m.w. 736.53): C, 48.92; H, 3.28; N, 7.61; Cr, 14.12%. Found: C, 48.69; H, 3.12; N, 7.35; Cr, 14.37%.

Synthesis of $[Cr_2(ox)_3(Mephen)_2]$ (3): This complex was obtained as pale-violet powder by the same procedure as described for complex **(1)**, except that Mephen (388.5 mg, 2 mmol) was used instead of bpy. Yield, 613 mg (81%); m.p. 337.°C. Anal. Calc. for $Cr_2C_{32}H_{20}N_4O_{12}$ (m.w. 756.52): C, 50.81; H, 2.66; N, 7.41; Cr, 13.75%. Found: C, 50.67; H, 2.51; N, 7.23; Cr, 13.51%.

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The melting points of the complexes were determined by a Model XT 7-1 micromelting point meter. The metal contents were determined using an ICP-4300 isoionic emission spectrophotometer. The infrared spectra were recorded with a Nicolet FT-IR spectrophotometer model 470 in KBr pellets. The electronic spectra (DMF solution) were measured on a Cary 300 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method, using $Hg[Co(SCN)_4]$ as the calibrant. Variable temperature magnetic susceptibilities were measured, using a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [18] for all the constituent atoms and effective magnetic moments were calculated by $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility, corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Synthesis and general properties of the binuclear complexes: One of the best strategies to design and synthesize discrete polynuclear species is the "complex as ligand" approach, *i.e.*, using mononuclear complexes, that contain potential donor groups, capable of coordinating to another metal ion [19,20]. In this study, our aim was to obtain binuclear chromium(III) complexes, therefore, this synthetic strategy was adopted. As the ligand complex we have selected tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$, as polyatomic bridging ligand, because it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes [15]. Simultaneously, 2,2′-bipyridine (bpy); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 5-methyl-1,10-phenanthroline (Mephen) were used as the terminal ligands. On the basis of elemental analyses and physical data, shown in Tables 1 and 2, respectively, it is reasonable to assume, that the reaction of potassium tris(oxalato)chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$) with $Cr(ClO_4)_3\cdot 6H_2O$ and the terminal ligand L (L = bpy, Me_2bpy, Mephen) in *ca.* 1:1:2 mole ratio yielded binuclear complexes of general formula $[Cr_2(ox)_3L_2]$, as expected. The general synthetic pathway for the complexation reaction taking place, may be represented as follows.

$$[Cr(ox)_3]^{3-} + Cr^{3+} + 2L \longrightarrow [Cr_2(ox)_3L_2] \qquad (L = bpy, Me_2bpy, Mephen)$$

These complexes are the first examples of binuclear chromium(III) complexes, bridged by tris(oxalato)chromate(III). For the three binuclear complexes, the molar conductance values in DMF solution (see Table 1) fall in the expected range for non-electrolytes [21]. This is consistent with the IR data and presumed structure of the complexes, shown in Figure 1. All the solid complexes are fairly stable in air and are soluble in some organic solvents, such as DMF, DMSO, acetonitrile and acetone, but attempts to obtain single crystals, suitable for X-ray structure determination, have so far been unsuccessful. However, the binuclear complexes were further characterized on the basis of the following results.

Infrared spectra: In order to clarify the mode of bonding, the IR spectrum of the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ was compared with the spectra of the three binuclear complexes. Since the IR spectra of all the three binuclear complexes are similar, the discussion is confined to the most important vibration in 400~4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the binuclear complexes, together with their assignments are given in Table 1. It is noteworthy that the spectrum of the mononuclear complex $K_3[Cr(ox)_3]\cdot 3H_2O$ only show typical of a bidentate coordination mode of the oxalato groups. However, the IR spectra of the three binuclear complexes exhibit bands corresponding to the bidentate oxalato ligand (*ca*. 1700, 1680, 1640 cm^{-1} [ν_{as}(CO)]; 790 cm^{-1} [δ(CO)]) and also the bridging oxalato ligand (*ca.* 1620 cm^{-1}[ν_{as}(CO)]; 1370, 1330 cm^{-1} [ν_s(CO)]) [11,13], suggesting that the oxalato groups of the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ coordinate with chromium(III) ions to form binuclear complexes. This is in accord with the presumed structure shown in Figure 1. On the other hand, the C–H deformation bands [δ(C–H)] of aromatic ring of the end-capping ligands (bpy, Me_2bpy, Mephen) are found in corresponding binuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the chromium(III) ions. The additional band observed at around 480 cm^{-1} due to ν(Cr–N) further supports this view. In addition, the band centered at *ca.* 1100 cm^{-1}, typical for ν(Cl–O) stretching of the perchlorate group [22], were not found for all the binuclear complexes.

Electronic spectra: In order to obtain further structural information of these binuclear complexes, the electronic spectra of the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ and the binuclear chromium(III) complexes were studied and assigned on the basis of a careful comparison of the latter with the former. As shown in Table 2, the electronic absorption spectra of the three binuclear complexes in DMF solution are quite similar. For all three binuclear complexes, a strong absorption at *ca.* 32×10^3 cm^{-1} found for all the complexes may be attributed to the charge-transfer absorption band [23]. Further investigation of these and similar systems is still required, in order to obtain a detailed assignment for charge transfer. In addition, three weaker bands (Table 2), which appear in the 16200~16250, 23410~23440 and 32790~32860 cm^{-1} regions, may be reasonably assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(\upsilon_1)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (υ_2) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (υ_3) transitions in the order of increasing energy, consistent with the presence of an octahedral coordination geometry [24] around the chromium(III) ion. According to the literature methods [24,25], some ligand field parameters, such as the interelectronic repulsion (Racah) parameters (B), crystal field splitting energy (10 Dq), nephelauxetic ratio (β) and the ligand field stabilization energy (LFSE) of these binuclear complexes may be evaluated from the observed bands (υ_1, υ_2, υ_3), and the calculated results are summarized in Table 2. As shown in this Table, the ligand field parameters are commensurate with octahedral geometry for the complexes, the values of $\beta < 1$ show strong covalent bonding of chromium(III) in these binuclear complexes [25].

Table 1. Physical data of the oxalato-bridged binuclear chromium(III) complexes.

Com-plexes	Λ_M	μ_{eff}	ν(ox) (bidentate)		ν(ox) (bridging)			
	($S \cdot cm^2 \cdot mol^{-1}$)	(μ_B)	ν_{as}(CO)	δ(CO)	ν_{as}(CO)	ν_s(CO)	ν(Cr–N)	δ(C–H)
(1)	8.2	5.39	1710, 1680, 1642	765	1629	1370, 1333	485	855, 723
(2)	7.8	5.41	1712, 1687, 1644	794	1625	1371, 1335	488	853, 721
(3)	8.0	5.36	1716, 1684, 1640	790	1623	1375, 1330	483	856, 728

(1) = $[Cr_2(ox)_3(bpy)_2]$, **(2)** = $[Cr_2(ox)_3(Me_2bpy)2]$, **(3)** = $[Cr_2(ox)_3(Mephen)_2]$

Table 2. Electronic spectral bands (cm^{-1}) and some coordination field parameters of the binuclear complexes.

Com-plexes	Assignments				Dq	B	β	LFSE
	ν_1 $^4A_{2g} \rightarrow {}^4T_{2g}$	ν_2 $^4A_{2g} \rightarrow {}^4T_{1g}$(F)	ν_3 $^4A_{2g} \rightarrow {}^4T_{1g}$(P)	CT (10^3 cm^{-1})	(cm^{-1})	(cm^{-1})		(kJ/mol)
(1)	16230	23410	32790	32.1	1623	501	0.546	231.9
(2)	16200	23440	32810	32.8	1620	510	0.556	231.5
(3)	16250	23420	32860	32.5	1625	502	0.547	232.2

Based on the composition of these complexes, their infrared spectra, electronic spectra, conductivity measurements and magnetic characterization (*vide infra*), these complexes are proposed to have an extended oxalato-bridged structure and to contain two chromium(III) ions bridged by the oxalato group, and each chromium(III) ion is in a six-coordinated octahedral environment, as shown in Figure 1. The plausible structure is further characterized by the following magnetic studies.

Magnetic studies: The observed magnetic moment per binuclear complex at room temperature, shown in Table 1, is slightly less than the spin-only value (5.48 B.M.) for binuclear chromium(III) (S = 3/2) complexes in the absence of an exchange interaction. This result reflects, that both chromium(III) ions of the binuclear complexes are in the S = 3/2 ground state and suggests the presence of a weak antiferroma-

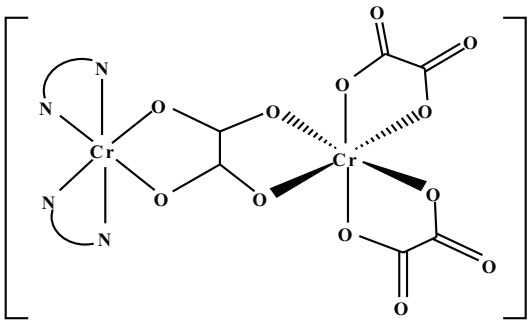

Figure 1. Plausible coordination environment of the complexes (N⌒N = bpy, Me_2bpy, Mephen).

gnetic spin-exchange interaction in these complexes [20,27]. Being interested in the magnetic behavior of these binuclear complexes, magnetic susceptibility data on polycrystalline samples for $[Cr_2(ox)_3(bpy)_2]$ **(1)** and $[Cr_2(ox)_3(Me_2bpy)_2]$ **(2)** complexes were collected between 4.2~300 K. The results are shown in Figure 2 in the form of plots of χ_M *vs.* T and μ_{eff} *vs.* T, where χ_M, μ_{eff} and T denote the magnetic susceptibility per molecule, the effective magnetic moment per molecule, and the absolute temperature, respectively. From Figure 2 it can be seen, that the magnetic behavior of the two complexes is similar. In the 30~300 K region, the curves of the effective magnetic moments (μ_{eff}) decrease steadily with decreasing temperature, but sharply decrease below *ca.* 30 K. This behavior is characteristic for a weak antiferromagnetic interaction between the two chromium(III) ions through the ox-bridge within each molecule [20,27]. This is consistent with the room-temperature magnetic moments of the complexes. Thus, as noted above, the observed magnetic behavior for complexes **(1)** and **(2)**, both at room-temperature and variable-temperature, clearly demonstrates the operation of an intramolecular antiferromagnetic spin-exchange interactions between the two chromium(III) ions through the ox-bridge within each molecule.

In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic susceptibility data were analysed by the spin Hamiltonian for isotropic binuclear magnetic exchange interaction, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where the exchange integral J is negative for an antiferromagnetic interaction and positive for a ferromagnetic. For the chromium(III)–chromium(III) ($S_1 = S_2 = 3/2$) system, the molar magnetic susceptibility is given by equation (1).

$$\chi_M = \frac{2N\beta^2 g^2}{KT}\left[\frac{14 + 5\exp(-6J/KT) + \exp(-10J/KT)}{7 + 5\exp(-6J/KT) + 3\exp(-10J/KT) + \exp(-12J/KT}\right] \quad (1)$$

Where χ_M is the molecular susceptibility per binuclear complex and the remaining symbols have their usual meaning. As shown in Figure 2, good least-squares fit to the experimental data were obtained with equation (1) for complexes **(1)** and **(2)**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$ are: $J = -9.73$ cm^{-1}, $g = 2.04$, $F = 2.6 \times 10^{-4}$ for **(1)**; and $J = -5.29$ cm^{-1}, $g = 2.01$, $F = 5.6 \times 10^{-4}$ for **(2)**. The results indicate, that these complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the chromium(III) ions within each molecule.

The complexes **(1)** and **(2)** have the same extended oxalato-bridge structures and their IR and electronic spectra are also similar. The only difference between **(1)** and **(2)** is that there are four methyl ($-CH_3$) substituents in the terminal ligands in the latter. However, their presence led to an exchange parameter J for **(1)** that is larger (absolute value) than that for complex **(2)**. This result suggests, that the methyl substituents in terminal ligands reduce antiferromagnetic spin-exchange interactions between metals ions. The influence of substituents in the terminal ligands on magnetic interac-

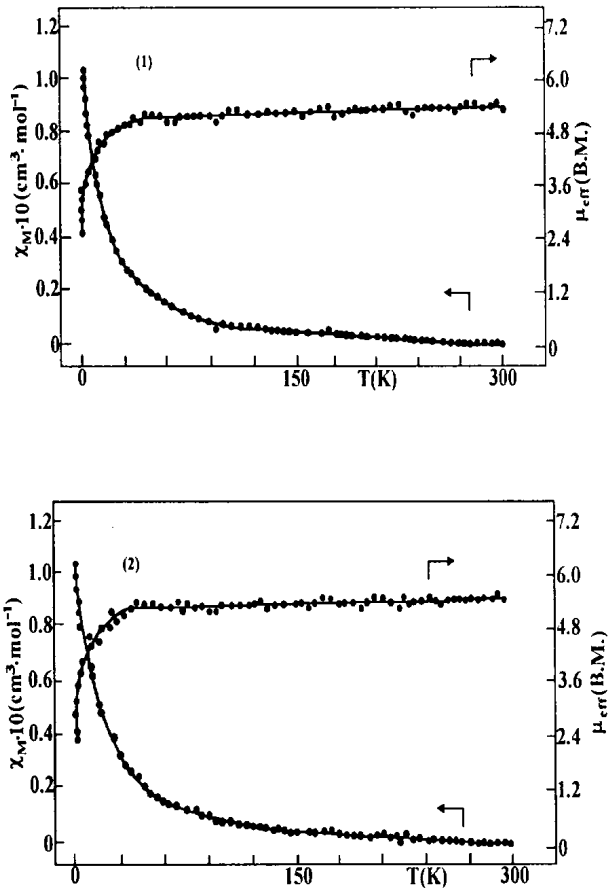

Figure 2. Plots of molar magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) *vs.* T for $[Cr_2(ox)_3(bpy)_2]$ **(1)** and $[Cr_2(ox)_3(Me_2bpy)_2]$ **(2)** complexes. The points denote the experimental data, the solid line represents the best least-squares fit to the experimental data using the parameters given in the text.

tions between the metal ions may be explained as follows. The substituent ($-CH_3$) in the terminal ligand (Me_2bpy) molecule is electron-supplying, which may affect both the electronic and molecular structure [28]. However, the terminal ligands are relatively rigid, and the structural influence of the methyl substituents on their J value is, therefore, relatively small and less important. However, the electron-supplying effect of the methyl group will increase the electron density on the metal ions. This will increase the electron-electron repulsion, thus, raising the metal orbital levels. This, in turn, will lead to a larger energy gap between the metal and the bridge orbitals and lower the delocalization of the metals orbitals towards the oxygen atoms of the bridge, so as to decrease the antiferromagnetic interactions. Indeed, further investigations on this and similar systems are still required, in order to get a deeper insight into the influence of the substituents in terminal ligands on magnetic interactions.

If we compare the present magnetic data with those previously reported for the analogous oxalato-bridged binuclear complexes [11,29,30], we found that the magnetic behavior of the present complexes is similar to those of other relevant oxalato-bridged binuclear complexes. It is known that the exchange interaction between the transition metal ions, propagated by the oxalate bridge, is strongly dependent on the geometry around the metal ions and the bridging mode of the oxalato anion. The geometry of the metal ion exerts a marked influence on the magnetic exchange interaction. Therefore, these small J values of complexes **(1)** and **(2)** may be brought out, mainly by the geometry structures of the complexes and the properties of the bridged-ligand [23].

Acknowledgments

This project was supported by the National Natural Science Foundation of China and the Natural Science Foundation of Shandong Province.

REFERENCES

1. Gatteschi D., Kahn O., Miller J.S. and Palacio F. (Eds.), "*Molecular Magnetic Materials*", NATO AST Series, Kluwer, Dordrecht, (1991).
2. Evans W.J., Clark R.D., Ansari M.A. and Ziller J.W., *J. Am. Chem. Soc*., **120**, 9555 (1998).
3. Guerriero P., Vigato P.A., Bunzli J.-C.G. and Moret E., *J. Chem. Soc., Dalton Trans*., 647 (1990).
4. Gunko Y.K., Hitchcock P.B. and Lappert M.F., *J. Chem. Soc., Chem. Commun*., 1843 (1998).
5. Piguet C., Rivara-Minten E., Bernardinelli G., Bunzli J.C.G. and Hopfgartner G., *J. Chem. Soc., Dalton Trans*., 421 (1997).
6. Costes J.P., Dahan F., Dupuis A., Lagrave S. and Laurent J.P., *Inorg. Chem*., **37**, 153 (1998).
7. Saalfrank R.W., Trummer S., Reimann U., Chowdhry M.M., Hampel F. and Waldmann O., *Angew. Chem., Int. Ed*., **39**, 3492 (2000).
8. Solomon F.I., Brunold T.C., Davis M.Z., Kemsley J.N., Lee S.-K., Skulan A.J., Yang Y.S. and Zhou J., *Chem. Rev*., **100**, 235 (2000).
9. Benelli C. and Gatteschi D., *Chem. Rev*., **102**, 2369 (2002).
10. Daiguebonne C., Guillou D., Kahn M.L., Kahn O., Oushoorn R.L. and Boubekeur K., *Inorg. Chem*., **40**, 176 (2001).
11. Cortes R., Urtiaga M.K., Lezama L., Arriortua M.I. and Rojo T., *Inorg. Chem*., **33**, 829 (1994).
12. Yu P., Journaux Y. and Kahn O., *Inorg. Chem*., **28**, 100 (1989).
13. Curtis N.F., *J. Chem. Soc*., 1584 (1968).
14. Coronado E., Gomez-Garcia C.J., Nuez A., Romero F.M., Rusanov E. and Stoeckli-Evans H., *Inorg. Chem*., **41**, 4615 (2002).
15. Coronado E., Galan-Malcaros J.R., Gimenez-Saiz C., Gomez-Garcia C.J. and Ruiz-Perez C., *Eur. J. Inorg. Chem*., 2290 (2003).
16. Brauer G. (Ed.), *Handbook of Preparative Inorganic Chemistry*, Academic Press, N.Y., 1372 (1965).
17. Baylar J.C. and Jones E.M., *Inorg. Synth*. (Ed.: H.S. Both), McGraw-Hill, NY, USA, 1939, Vol. 1, p. 35.
18. Selwood P.W., "*Magnetochemistry*", Interscience, N.Y., pp. 78–91 (1956).
19. Sinn E., in "*Biological and Inorganic Copper(II) Chemistry*", K.D. Karlin and J. Zubieta (Eds.), Adenine Press, Guilderland, N.Y. (1986).
20. Li Y.T., Yan C.W., Miao S.H. and Liao D.Z., *Polyhedron*, **15**, 2491 (1998).
21. Geary W.J., *Coord. Chem. Rev*., **7**, 81 (1971).
22. Nakamoto K., "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", Wiley, N.Y. (1986).

23. Kahn O., *Angew. Chem., Int. Edit. Engl*., **24**, 384 (1985).
24. Lever A.B.P. , "*Inorganic Electronic Spectroscopy*", Elsevier Science Publishers B. V., Amsterdam, Oxford, N.Y., Tokyo (1984).
25. Jørgensen C.K., *Progr. Chem*., **4**, 101 (1962).
26. Singh B. and Sahaip P., *Synth. React. Inorg. Met.-Org. Chem* ., **28**, 61 (1998).
27. Lambert S.L., Spiro C.L., Gagne R.R. and Hendrickson D.N., *Inorg. Chem.*, **21**, 68 (1982).
28. Brewer G.A. and Sinn E., *Inorg. Chem*., **26**, 1529 (1987).
29. Julve M., Verdaguer M., Gleizes A., Philoche-Levisalles M. and Kahn O., *Inorg. Chem.*, **23**, 3808 (1984).
30. Bencini A., Bianchi A., Poli P., Garcia-Espana E., Julve M. and Marcelino V., *J. Chem. Soc., Dalton Trans*., **7**, 2213 (1990).