SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF NOVEL COMPLEX [μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O (ept = *N*-(2-AMINOETHYL)PROPANE-1,3-DIAMINE)

Zdeněk SMÉKAL[a1,*], Jiří KAMENÍČEK[a2], Ingrid SVOBODA[b] and Albert ESCUER[c]

[a] *Department of Inorganic and Physical Chemistry, Palacký University, 771 47 Olomouc, Czech Republic; e-mail: [1] smekal@risc.upol.cz, [2] kamen@risc.upol.cz*
[b] *Fachbereich Materialwissenschaft, Technische Universität Darmstadt, 642 87 Darmstadt, Germany; e-mail: de0s@hrzpub.tu-darmstadt.de*
[c] *Departament de Química Inorgànica, Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain; e-mail: aescuer@kripto.qui.ub.es*

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The novel complex [μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O (ept = *N*-(2-aminoethyl)-propane-1,3-diamine) was obtained by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with *N*-(2-aminoethyl)propane-1,3-diamine and $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ in water. This compound was characterized by IR, UV-VIS and EPR spectroscopies and magnetic measurement. Single-crystal X-ray structure analysis revealed that the title complex has a one-dimensional polymeric structure containing hexacoordinate iron(II) with five cyanide ligands (two of them, in *trans* position, bridging) and one nitrosyl group, and pentacoordinate copper(II) with *N*-(2-aminoethyl)propane-1,3-diamine and two sites occupied by bridging cyanide ligands. Magnetic investigation revealed a very weak antiferromagnetic interaction between the copper atoms (superexchange interaction parameter $J = -1.7(1)$ cm^{-1}; $H = -JS_iS_{i+1}$) within the chain through the diamagnetic $[Fe(CN)_5NO]^{2-}$ ions.

Keywords: Copper(II); Iron(II); Cyanide-bridged complexes; Diamines; Nitroprussides; Cyanides; Magnetic properties; Crystal structure.

Consistently with the diversity of crystal structures and interesting properties, especially in the context of their magnetic behaviour, cyanide complexes unceasingly keep attracting much attention in coordination chemistry[1–8]. During the last few years, effects have been directed towards the synthesis of molecular-based magnets, in particular Prussian blue-like ones[9,10]. Prussian blue itself is also a ferromagnet with $T_C = 5.6$ K (ref.[11]). Considering that the magnetic interactions are mediated by diamagnetic $[Fe(CN)_6]^{4-}$ anions, it is useful to investigate the magnetic interactions between paramagnetic transition metal ions connected by a diamagnetic anion, namely $[Fe(CN)_5NO]^{2-}$. Since copper(II) is normally four-, five- or

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six-coordinate, it was anticipated that the coupling of a copper(II) amine to the $[Fe(CN)_5NO]^{2-}$ ion might lead to the formation of a novel family of magnetic compounds.

Recently, some nitroprusside-bridged polymeric complexes have been reported[12–14]. A magnetic study revealed a very weak antiferromagnetic interaction between nickel and copper atoms through the nitroprusside anion in $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Ni(en)}_2]_n \cdot n H_2O$ (en = ethylenediamine)[12] (superexchange interaction parameter $J = -0.47\ \text{cm}^{-1}$) and $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2]_n$ (ref.[13]) ($J = -1.06\ \text{cm}^{-1}$), respectively. The structure of $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2]_n$ consists of alternating $\{Cu(en)_2\}^{2+}$ and $[Fe(CN)_5NO]^{2-}$ moieties linked with two (in *cis* positions in the anion and in *trans* positions in the cation) cyanide ligands of the $[Fe(CN)_5NO]^{2-}$ dianion, giving rise to an one-dimensional chain structure. This complex was isolated from the aqueous system $Cu(II)en[Fe(CN)_5NO]^{2-}$. From the same system, but using copper(II) perchlorate instead of copper(II) chloride, a trinuclear complex $[Cu(en)_2][Fe(CN)_4\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2\text{-}\mu\text{-(NC)-Fe(CN)}_4\text{(NO)}]$ was isolated[15]. In a previous study we prepared and characterized a binuclear complex $[Fe(CN)_4\text{(NO)-}\mu\text{-(CN)-Cu(pn)}_2]$ (ref.[16]) (pn = 1,2-diaminopropane), which the Cu(II) centre pentacoordinated by five nitrogen atoms. With the aim to prepare novel low-dimensional solids, we have extended the series of amine ligands with tridentate *N*-(2-aminoethyl)propane-1,3-diamine (ept), that was reacted with $Cu(ClO_4)_2 \cdot 6H_2O$ and $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. The title complex obtained from this mixture will be introduced hereinafter.

EXPERIMENTAL

Chemicals and Methods

All chemicals (Aldrich, reagent grade) were used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out with a EA 1108 CHN analyser of Fisons Instruments. Diffuse-reflectance electronic spectrum was recorded on a Specord M 40 spectrophotometer and IR spectrum on a Specord IR 80 spectrometer (Carl Zeiss, Jena), both by the Nujol technique. Magnetic properties were measured on polycrystalline sample in the temperature range of 4.8–299 K with a conventional susceptometer. Diamagnetic corrections were taken from Pascal constants. EPR spectra were recorded on a Bruker ES 200 spectrometer at X-band frequency at room temperature and at 4 K.

Crystals of $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(ept)}]_n \cdot 4n H_2O$ (**1**) suitable for the single-crystal X-ray study were grown from water by slow evaporation at room temperature. The reflections were collected on a Nonius CAD4 diffractometer using the ω–2θ scan mode. Stability of the crystal was checked by monitoring three standards after every 120 reflections (decay was 3.4%). Unit-cell parameters were determined by least-squares refinement of 25 reflections in the range $3.3° < \theta < 14.2°$.

The structure was solved by direct methods (SHELXS97)[17] with anisotropic refinement[18]. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares procedure with the weight $w = 1/[\sigma^2(F_o^2) + (0.1370P)^2 + 1.6499P]$, where $P = (F_o^2 + 2F_c^2)/3$. Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC-137655. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

The crystal data and structure refinement details for [μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O are given in Table I. Table II summarizes selected bond lengths and angles.

TABLE I
Crystal data and structure refinement for [μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O (**1**)

Formula	$C_{10}H_{15}CuFeN_9O_5$
M_w	460.70
Crystal size, mm	0.33 × 0.30 × 0.25
T, K	300(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	12.713(2)
b, Å	10.792(3)
c, Å	14.643(2)
α, °	90
β, °	113.01(2)
γ, °	90
U, Å^3; Z	1 849.2(6); 4
D_c, g cm^{-3}	1.655
λ, Å	0.71069
μ, mm^{-1}	1.976
F(000)	932
θ range for data collection, °	1.80–26.09
Index ranges	$-15 \le h \le 3$; $-13 \le k \le 0$; $-17 \le l \le 17$
Reflections collected; unique	4 582; 3 645 (R(int) = 0.0360)
Refinement method	Full-matrix least-squares on F_o^2
Data; restraints; parameters	3 645; 0; 229
Goodness-of-fit^c on F^2	0.993
Final R indices [$I > 2\sigma(I)$]^{a,b}	$R1 = 0.0576$, $wR2 = 0.1633$
R indices (all data)^{a,b}	$R1 = 0.0726$, $wR2 = 0.1778$
Largest difference peak and hole, e Å^{-3}	1.335, –1.077

[a] $R1 = \Sigma\left|F_o - F_c\right| / \Sigma\left|F_c\right|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97, ref.[18]).

Synthesis

[μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O (**1**). A solution of Cu(ClO$_4$)$_2$·6H$_2$O (1.0 g, 2.70 mmol) and *N*-(2-aminoethyl)propane-1,3-diamine (0.34 ml, 2.70 mmol) in 50 ml water was added to a solution of Na$_2$[Fe(CN)$_5$NO]·2H$_2$O (0.80 g, 2.69 mmol) in 50 ml water. A small amount of the solid formed was discarded. The black polycrystalline product, obtained from the reaction mixture on one-day standing, was filtered off, washed with water and dried in air. The yield was 0.5 g (40%). μ_B (298 K) = 2.02. For $C_{10}H_{15}CuFeN_9O_5$ (460.7) calculated: 25.62% C, 4.95% H, 26.89% N; found: 27.68% C, 4.59% H, 28.86% N.

RESULTS AND DISCUSSION

Single-crystal X-ray structure analysis of complex **1** revealed a cyanide-bridged polymeric chain structure in which iron(II) is coordinated by five cyanide ligands (two of them, in *trans* position, bridging) and one nitrosyl group (FeC$_5$N moiety), and copper(II) is coordinated by tridentate

TABLE II
Selected bond lengths (in Å) and angles (in °) for [μ-(NC)-Fe(CN)$_3$(NO)-μ-(CN)-Cu(ept)]$_n$·4nH$_2$O (**1**)

Cu(1)–N(1)	1.987(5)	Fe(1)–C(9)	1.931(4)
Cu(1)–N(6)	1.994(4)	Fe(1)–C(7)	1.930(5)
Cu(1)–N(3)	1.994(4)	Fe(1)–C(10)	1.930(5)
Cu(1)–N(2)	2.009(4)	Fe(1)–C(8)	1.932(5)
Cu(1)–N(10a)[a]	2.367(4)	Fe(1)–C(6)	1.930(5)
Fe(1)–N(5)	1.651(4)	N(10)–Cu(1b)[b]	2.367(4)
N(1)–Cu(1)–N(6)	89.42(19)	N(5)–Fe(1)–C(10)	94.82(19)
N(1)–Cu(1)–N(3)	172.41(19)	C(9)–Fe(1)–C(10)	90.44(19)
N(6)–Cu(1)–N(3)	90.46(17)	C(7)–Fe(1)–C(10)	86.9(2)
N(1)–Cu(1)–N(2)	84.3(2)	N(5)–Fe(1)–C(8)	178.90(19)
N(6)–Cu(1)–N(2)	167.5(2)	C(9)–Fe(1)–C(8)	84.93(19)
N(3)–Cu(1)–N(2)	94.34(19)	C(7)–Fe(1)–C(8)	85.8(2)
N(1)–Cu(1)–N(10a)[a]	93.57(19)	C(10)–Fe(1)–C(8)	85.2(2)
N(6)–Cu(1)–N(10a)[a]	95.88(17)	N(5)–Fe(1)–C(6)	94.47(18)
N(3)–Cu(1)–N(10a)[a]	93.99(17)	C(9)–Fe(1)–C(6)	92.97(19)
N(2)–Cu(1)–N(10a)[a]	95.3(2)	C(7)–Fe(1)–C(6)	88.2(2)
N(5)–Fe(1)–C(9)	93.97(18)	C(10)–Fe(1)–C(6)	169.86(19)
N(5)–Fe(1)–C(7)	95.3(2)	C(8)–Fe(1)–C(6)	85.6(2)
C(9)–Fe(1)–C(7)	170.57(19)		

Symmetry transformations used to generate equivalent atoms: [a] $-x + 1/2$, $y - 1/2$, $-z + 1/2$; [b] $-x + 1/2$, $y + 1/2$, $-z + 1/2$.

N-(2-aminoethyl)propane-1,3-diamine and two bridging cyanide ligands (CuN_5 moiety). The structure of the studied complex is presented in Chart 1 and Fig. 1. The monomeric unit is shown in Fig. 2. Selected bond lengths and angles are given in Table II. The copper atom is pentacoordinated by two cyanide-nitrogen and three ept-nitrogen atoms in a distorted square-pyramidal arrangement with one cyanide nitrogen atom and three ept-nitrogen atoms bonded in the plane and one cyanide-nitrogen atom as

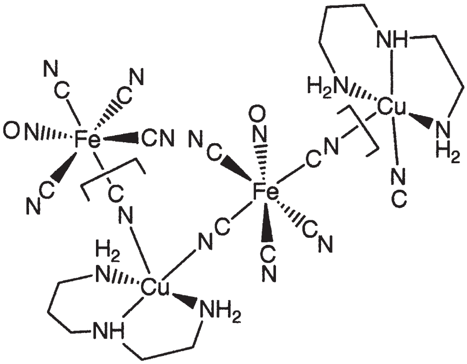

CHART 1

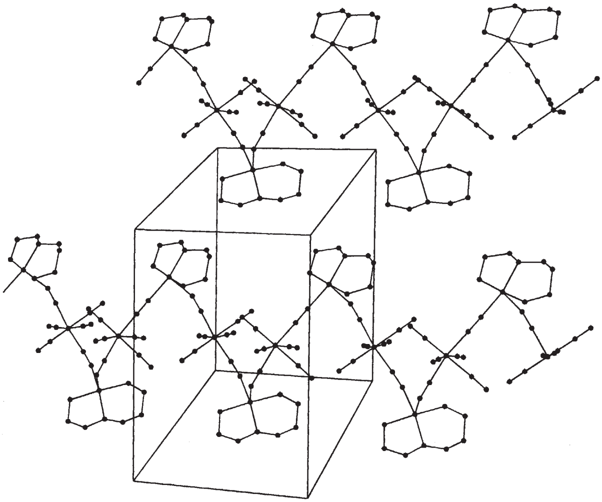

FIG. 1

Polymeric chain structure of $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(ept)}]_n \cdot 4nH_2O$ (**1**). The molecules of water are omitted for clarity axial ligand. The in-plane Cu(1)–N bond lengths range from 1.987(5) to 2.009(4) Å and the axial Cu(1)–N(10a) bond distance (2.367(4) Å) is significantly longer then the in-plane Cu(1)–N bonds. One oxygen atom from a water molecule (O4) is at a semicoordination distance, around 2.77 Å, and the coordination of Cu(1) may also be envisaged as pseudo-octahedral. The cyanide groups act as ligands, bridging the Cu(II) and Fe(II) centres in Fe–C≡N–Cu chains. The mean bond lengths Fe–C (1.931 Å), Fe–N (1.651(4) Å), C–N (1.138 Å) and N–O (1.133(5) Å) in the pseudooctahedral $[Fe(CN)_5NO]^{2-}$ moiety are in good agreement with the reported values for other nitroprusside metal salts[12–16]. The higher electronegativity of the nitrosyl group compared to that of the cyanide groups causes distortion of the octahedral geometry. The C–Fe–NO angles are larger than 90° whereas the C–Fe–C angles are smaller than 90°. The value for Fe–N–O is close to straight angle (178.8(3)°). The intramolecular distances Cu(II)···Fe(II) and Cu(II)···Cu(II) are 4.993(5) and 9.458(5) Å, respectively.

The studied complex **1** contains a cyanide-bridged chain like the analogous complex $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2]_n$ (ref.[13]) which is a polymer with one-dimensional chain structure with two cyanide groups serving as bridges between the Cu(II) and Fe(III) centres. Both structures differ in the coordination number of copper atom – five for complex **1** and six for $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2]_n$, and in the arrangement of the bridging cyanide groups – *trans* fashion for complex **1** and *cis* fashion for $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(en)}_2]_n$.

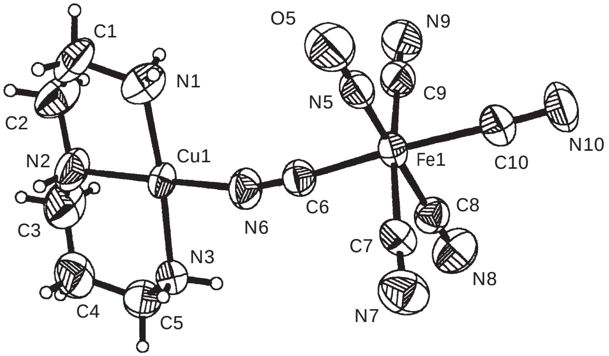

FIG. 2
ORTEP representation of a single unit of $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(ept)}]_n\cdot 4n H_2O$ (**1**) with the atom-labelling scheme. The molecules of water are omitted for clarity

In the IR spectrum of **1** characteristic bands for ν(CN) and ν(NO) vibrations were assigned. The nitroprusside anion shows the NO stretching frequency at 1 942 cm^{-1}, indicating an NO^+ complex of iron(II) with extensive π bonding, and characteristic ν(CN) vibrations at 2 144, 2 158 and 2 174 cm^{-1} ($Na_2[Fe(CN)_5NO]\cdot 2H_2O$) (refs[15,19]). In the IR spectrum of the studied complex **1**, the strong bands at 2 140 and 2 176 cm^{-1} region may be attributed to ν(CN) modes. Very strong broad band at 1 940 cm^{-1} is reasonably assigned to the NO stretching vibration, which is almost the same as that in the nitroprusside ion.

The UV-VIS spectrum of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ does not provide information about the electronic structure of iron(II)[20]. Only CT band can be observed for $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (24 500 cm^{-1})[19]. The UV-VIS spectra of the studied complexes are probably superpositions of spectra of $[Fe(CN)_5NO]^{2-}$ and the Cu(II) moiety. The UV-VIS absorption spectra of Cu(II) complexes are characterized by a strong band in the range 13 000–18 000 cm^{-1}, corresponding to *d*-*d* transitions[21]. In compound **1**, the maximum at 17 500 cm^{-1} can be assigned to a *d*-*d* band.

Due to the diamagnetic nature of the $[Fe(CN)_5NO]^{2-}$ anion, the paramagnetism of the prepared nitroprusside complex is caused by copper(II). The observed value of magnetic moment (2.02 μ_B) at room temperature agrees with the literature data for magnetically diluted Cu(II) compounds (1.9–2.2 μ_B)[22]. The temperature dependence of the $\chi_m T$ (χ_m = molar magnetic susceptibility) of complex **1** per a CuFe unit is shown in Fig. 3. At room temperature (290 K),

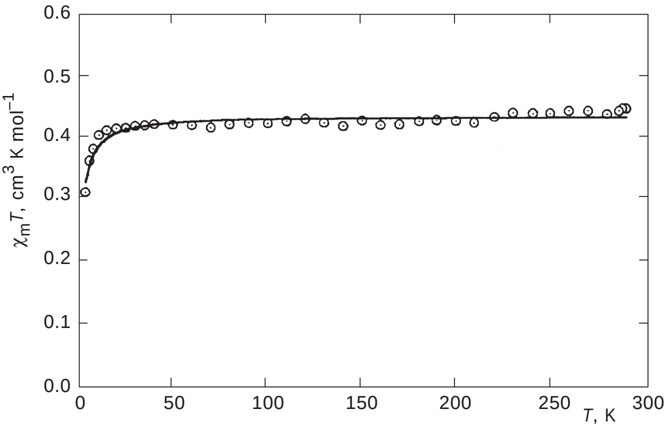

FIG. 3

Temperature dependence of $\chi_m T$ for $[\mu\text{-(NC)-Fe(CN)}_3\text{(NO)-}\mu\text{-(CN)-Cu(ept)}]_n\cdot 4nH_2O$ (**1**). The solid line denotes a theoretical fit of the data with the parameters listed in the text the $\chi_m T$ value 0.45 cm^3 K mol^{-1} is close to that for an isolated copper(II) ion ($S = 1/2$) with diamagnetic iron(II) ion ($S = 0$). With decreasing temperature, the $\chi_m T$ value remains almost constant until 12 K and then it decreases sharply, giving the minimum value of 0.31 cm^3 K mol^{-1} at 4.8 K. The drop in $\chi_m T$ at low temperatures indicates the presence of a weak antiferromagnetic coupling between the copper(II) ions. We attempted to reproduce theoretically the experimental susceptibility by using the expression for a classic-spin Heisenberg chain based in the Hamiltonian $H = -JS_iS_{i+1}$, in which J is the superexchange interaction parameter and S corresponds to the local spin, scaled to a real spin $S = 1/2$, which is valid for an antiferromagnetic coupling. The fit[23] to the experimental data gave the parameters $J = -1.7(1)$ cm^{-1} and $g = 2.163(4)$. The EPR spectra of complex **1** recorded at room temperature and 4 K are very similar, consisting of single centred at $g = 2.084$ (room temperature) and 2.09 (4 K). Complex **1** shows a very weak coupling, as may be expected from the diamagnetic –NC–Fe–CN– bridge. The weak magnetic exchange can be understood considering the large copper–copper distance.

If we compare the magnetic behaviour ($J = -1.7(1)$ cm^{-1}) of the present complex with that of a two-dimensional complex $[Fe(\mu\text{-}CN)_6\{Cu(ept)\}_3](ClO_4)_2\cdot 5H_2O$ (ref.[8]), we can see that both compounds contain the $-Cu^{II}(ept)-NC-Fe^{II}-CN-Cu^{II}(ept)-$ moiety, but coupling between the copper atoms was found at 4.8 K only for complex **1**. In order to obtain a correlation between magnetic properties and structure, more examples of this type of complexes are needed. We will continue to modify the coordination sphere of the copper(II) centre and thus the magnetic properties by replacing sterically demanding amine ligands.

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REFERENCES

1. Ferlay S., Mallah T., Ouahes R., Veillet P., Verdaguer M.: *Inorg. Chem.* **1999**, *38*, 229.
2. Re N., Crescenzi R., Floriani C., Miyasaha H., Matsumoto N.: *Inorg. Chem.* **1998**, *37*, 2717.
3. El Fallah M. S., Ribas J., Solans X., Font-Bardia M.: *J. Chem. Soc., Dalton Trans.* **2001**, 247.
4. Ohba M., Okawa H., Fukita N., Hashimoto Y.: *J. Am. Chem. Soc.* **1997**, *119*, 1011.
5. Ohba M., Usuki N., Fukita N., Okawa H.: *Inorg. Chem.* **1998**, *37*, 3349.
6. Kou H. Z., Liao D. Z., Jiang Z. H., Yan S. P., Wu Q. J., Gao S., Wang G. L.: *Inorg. Chem. Commun.* **2000**, *3*, 151.

7. Verdaguer M., Bleuzen A., Marvaud V., Vaissermann J., Seuleiman M., Desplanches C., Scuiller A., Train C., Garde R., Gelly G., Lomenech C., Rosenman I., Veillet P., Cartier R., Villain F.: *Coord. Chem. Rev.* **1999**, *190–192*, 1023.
8. Trávníček Z., Smékal Z., Escuer A., Marek J.: *New J. Chem.* **2001**, *25*, 655.
9. Bleuzen A., Lomenech C., Escax V., Villain F., Varret F., Cartier C., Verdaguer M.: *J. Am. Chem. Soc.* **2000**, *122*, 6648.
10. Cartier C., Villain F., Bleuzen A., Arrio M. A., Sainctavit P., Lomenech C., Escax V., Baudelet F., Dartyge E., Gallet J. J., Verdaguer M.: *J. Am. Chem. Soc.* **2000**, *122*, 6653.
11. Herren F., Fischer P., Ludi A., Haly W.: *Inorg. Chem.* **1980**, *19*, 956.
12. Shyu H. L., Wei H. H., Wang Y.: *Inorg. Chim. Acta* **1997**, *258*, 81.
13. Kou H. Z., Wang H. M., Liao D. Z., Cheng P., Jiang Z. H., Yan S. P., Huang X. Y., Wang G. L.: *Aust. J. Chem.* **1998**, *51*, 661.
14. Chen Z. N., Wang J. L., Qiu J., Miao F. M., Tang W. X.: *Inorg. Chem.* **1995**, *34*, 2255.
15. Zhan S., Chen X., Vij A., Guo D., Meng Q.: *Inorg. Chim. Acta* **1999**, *292*, 157.
16. Smékal Z., Trávníček Z., Marek J., Nádvorník M.: *Aust. J. Chem.* **2000**, *53*, 225.
17. Sheldrick G. M.: *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1990**, *46*, 467.
18. Sheldrick G. M.: *SHELXL97, Program for Crystal Structure Refinement*. University of Göttingen, Göttingen 1997.
19. Wilkinson G., Gillard R. D., McCleverty J. A.: *Comprehensive Coordination Chemistry*, Vol. 4. Pergamon Press, Oxford 1987.
20. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*. Wiley, New York 1966.
21. Lever A. B. P.: *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam–London–New York 1968.
22. Greenwood N. N., Earnshow A.: *Chemistry of the Elements*. Informatorium, Prague 1993.
23. Estes W. E., Gavel D. P., Hatfield W. E., Hodgson D.: *Inorg. Chem.* **1978**, *17*, 1415.