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Syntheses, crystal structures and fluorescence emission of one-dimensional and mononuclear complexes generated from zinc(II) and carbamyldicyanomethanide

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Abstract

A one-dimensional chain complex $\{[Zn(cda)_2(CH_3OH)_2]\cdot 4CH_3OH\}_\infty$ (*cda* = carbamyldicyanomethanide anion) (**1**) and a mononuclear complex $[Zn(cda)_2(H_2O)_4]\cdot 2H_2O$ (**2**) have been synthesized and their crystal structures determined by X-ray crystallography. The zinc(II) ion in **1** is bridged by double $\mu_{1,5}$-*cda* bridging ligands and the uncoordinated methanol molecules are trapped in the cavities. Compound **2** is a mononuclear complex and the zinc(II) ion is coordinated by two nitrile-nitrogen atoms and four aqua ligands. The complexes show fluorescence both in the solid state and in solution.

Keywords: Syntheses; Crystal structures; Zinc complexes; Polynitrile ligands; Fluorescence

1. Introduction

Much research interest has been focused on the crystal engineering of coordination compounds that may afford new materials with useful properties such as catalytic, micro-porosity, electrical conductivity, nonlinear optical activity and co-operative magnetic behavior [1,2]. Polynitrile compounds such as tricyanomethanide, dicyanamide, 7,7,8,8-tetracyanoquinodimethane, 1,2,4,5-tetracyanobenzene and tetracyanoethene display versatile bridging modes and many coordination compounds have been constructed from such polynitriles and metal ions [3–15]. In terms of physical properties the focal point is on the magnetic interaction between polynitrile-bridged metal ions with only limited studies dealing with electrical conductance [16] and optical properties [17], and no fluorescence study has been reported. Owing to its chemical structure the polynitrile ligand *cda* should be a very useful bridging ligand and can be used to construct coordination compounds with new structures and physical properties. Although complexes of *cda* with Zn(II), Co(II), Ni(II), Cu(II) are known [18,19], their crystal structures and physical properties have not been reported. In view of the excellent physical properties of polynitrile compounds, we synthesized and characterized a few lanthanide and transition metal complexes with *cda* as a bridging ligand and a terminal ligand [20,21]. The spectral measurements of the complexes indicate fluorescent emission both in the solid state and in solution. Here we report the crystal structures and the fluorescent property of the titled complexes.

2. Experimental

2.1. Materials

Sodium carbamyldicyanomethanide (Na(*cda*)) was prepared according to the literature [22], and other chemicals are analytical grade and used without further purification.

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2.2. *Physical measurements*

The IR spectra were recorded with a Shimadzu-corporation 408 IR spectrophotometer using KBr discs. C, H and N elemental analyses were carried out on a Carlo-Erba Elemental analyzer, Model 1106. The fluorescence spectra were obtained on a Perkin–Elmer LS-50 fluorescence spectrophotometer.

2.3. *X-ray crystallography*

The determination of the crystal structures was carried out on a Bruker Smart-1000 CCD using graphite-monochromated Mo Kα radiation (0.71073 Å). Data reduction and structure refinement were performed using the SHELXL-97 program system. Details of crystal parameters and data collection are listed in Table 1. The selected bond lengths and angles are listed in Table 2.

2.4. *Synthesis of the complexes*

2.4.1. *$\{[Zn(cda)_2(CH_3OH)_2]\cdot 4CH_3OH\}_\infty$ (**1**)*

Na(*cda*) (0.3025 g, 2.31 mmol) and $Zn(ClO_4)_2\cdot 6H_2O$ (0.4305 g, 1.16 mmol) were each dissolved in 15 cm^3 MeOH and then the two kinds of solutions were mixed together and placed in a sealed vessel that contained a saturated calcium chloride solution in MeOH. Colorless transparent single-crystals were obtained after a few of days at room temperature (r.t.). The obtained crystal easily decomposed in air at r.t. *Anal.* Found: C, 35.2; H, 5.6; N, 18.1; Zn, 14.1. Calc. for $C_{14}H_{28}N_6O_8Zn$: C, 35.5; H, 6.0; N, 17.7; Zn, 13.8%.

Table 1
Crystallographic data and collection parameters for complexes **1** and **2**

	1	**2**
Chemical formula	$C_{14}H_{28}N_6O_8Zn$	$C_8H_{16}N_6O_8Zn$
Crystal system	triclinic	monoclinic
Space group	P_1	$P_{2(1)}/n$
a (Å)	7.218(2)	9.402(3)
b (Å)	7.391(2)	7.413(2)
c (Å)	12.394(4)	12.042(4)
α (°)	80.788(4)	90
β (°)	76.130(4)	108.682(4)
γ (°)	60.871(3)	90
V (Å^3)	559.9(3)	795.1(4)
D_{calc} (g cm^{-3})	1.405	1.627
Absorption coefficient (mm^{-1})	1.146	1.595
$F(000)$	248	400
Crystal dimension (mm)	$0.60\times 0.50\times 0.40$	$0.50\times 0.35\times 0.35$
T Range for data collection (°)	3.16–25.02	2.41–25.03
Limiting indices	$-5\leq h\leq 8$, $-8\leq k\leq 8$, $-14\leq l\leq 14$	$-11\leq h\leq 7$, $-8\leq k\leq 8$, $-14\leq l\leq 13$
Reflections collected/unique [R_{int}]	2933/2363 [0.0144]	3970/1406 [0.0200]
Data/restraints/parameters	2363/28/374	1406/6/138
Final R indices [$I>2\sigma(I)$]	$R_1=0.0260$, $wR_2=0.0637$	$R_1=0.0267$, $wR_2=0.0727$
R indices (all data)	$R_1=0.0297$, $wR_2=0.0656$	$R_1=0.0314$, $wR_2=0.0750$
Goodness-of-fit on F^2	1.008	1.138
Largest difference peak and hole (e Å^{-3})	0.240 and −0.247	0.307 and −0.586

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

Complex **1**			
Bond lengths			
Zn(1)–O(3)	2.083(7)	Zn(1)–O(4)	2.099(7)
Zn(1)–N(5)	2.109(6)	Zn(1)–N(3)	2.120(8)
Zn(1)–N(2)	2.128(7)	Zn(1)–N(6)	2.163(7)
Bond angles			
O(3)–Zn(1)–O(4)	177.9(4)	O(3)–Zn(1)–N(5)	89.4(3)
O(4)–Zn(1)–N(5)	91.1(3)	O(3)–Zn(1)–N(3)	90.7(3)
O(4)–Zn(1)–N(3)	88.8(3)	N(5)–Zn(1)–N(3)	178.9(4)
O(3)–Zn(1)–N(2)	91.2(3)	O(4)–Zn(1)–N(2)	90.8(3)
N(5)–Zn(1)–N(2)	88.0(3)	N(3)–Zn(1)–N(2)	90.9(3)
O(3)–Zn(1)–N(6)	87.0(3)	O(4)–Zn(1)–N(6)	91.0(3)
N(5)–Zn(1)–N(6)	93.4(3)	N(3)–Zn(1)–N(6)	87.7(3)
N(2)–Zn(1)–N(6)	177.7(5)		
Complex **2**			
Bond lengths			
Zn(1)–O(2)	2.0781(16)	Zn(1)–N(2)	2.115(2)
Zn(1)–O(3)	2.1245(15)		
Bond angles			
O(2A)–Zn(1)–O(2)	180.0	O(2A)–Zn(1)–N(2A)	89.56(7)
O(2)–Zn(1)–N(2A)	90.44(7)	O(2A)–Zn(1)–N(2)	90.44(7)
O(2)–Zn(1)–N(2)	89.56(7)	N(2A)–Zn(1)–N(2)	180.0
O(2A)–Zn(1)–O(3A)	91.95(7)	O(2)–Zn(1)–O(3A)	88.05(7)
N(2A)–Zn(1)–O(3A)	91.91(7)	N(2)–Zn(1)–O(3A)	88.09(7)
O(2A)–Zn(1)–O(3)	88.05(6)	O(2)–Zn(1)–O(3)	91.95(7)
N(2A)–Zn(1)–O(3)	88.09(7)	N(2)–Zn(1)–O(3)	91.91(7)
O(3A)–Zn(1)–O(3)	180.0		

2.4.2. *$[Zn(cda)_2(H_2O)_4]\cdot 2H_2O$ (**2**)*

A solution of Na(*cda*) (0.3337 g, 2.54 mmol in 15 cm^3 H_2O) was added to a solution of $Zn(ClO_4)_2\cdot 6H_2O$ (0.4732 g, 1.27 mmol in 15 cm^3 H_2O) and the mixture was stirred for a few minutes. Colorless transparent crystals of **2** were obtained after a few days. *Anal.* Found: C, 24.5; H, 4.3; N, 21.9; Zn, 16.5. Calc. for $C_8H_{16}N_6O_8Zn$: C, 24.6; H, 4.1; N, 21.6; Zn, 16.8%.

3. Results and discussion

3.1. *IR spectra*

Compared with the band of sodium *cda*, the characteristic bands of $-C\equiv N$ have shifted from 2160 and 2200 cm^{-1} to 2190 and 2240 cm^{-1} for **1** and to 2185

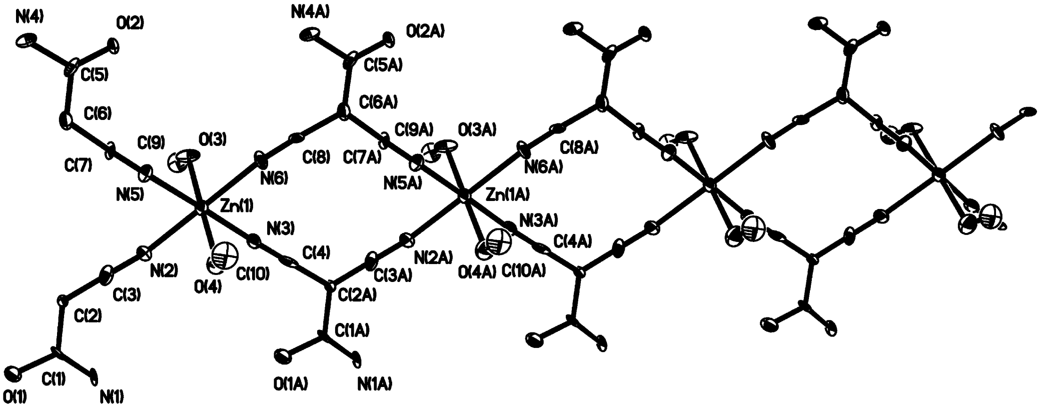

Fig. 1. The coordination and 1-D chain diagram of $\{[Zn(cda)_2(CH_3OH)_2]\cdot 4CH_3OH\}_\infty$ (**1**) with atom numbering scheme.

and 2220 cm^{-1} for **2**. The sharp peaks at 3220, 3320 and 3455 cm^{-1} for $\nu(NH_2)$ appear as a broad bands from 3170 to 3400 cm^{-1} for **1** and from 3100 to 3450 cm^{-1} for **2**. The intense bands at 1440, 1560 and 1660 cm^{-1} for $-CONH_2$ have shifted to 1420, 1560 and 1630 cm^{-1} for **1** and to 1430, 1510 and 1630 cm^{-1} for **2**, and at the same time these bands became broad and the absorption intensity decreased.

3.2. Crystal structures

3.2.1. $\{[Zn(cda)_2(CH_3OH)_2]\cdot 4CH_3OH\}_\infty$ (1)

Fig. 1 shows the coordination diagram of **1** with the atom numbering scheme and the one-dimensional chain structure. The Zn(II) ion is coordinated by two oxygen atoms from two methanol molecules and four nitrogen atoms from nitrile groups. The coordination bond lengths range from 2.083(7) to 2.163(7) Å and the associated angles range from 87.0(3)° to 178.9(4)°, as shown in Table 2. Fig. 1 also displays the formation of a one-dimensional chain along the *b* axis through the

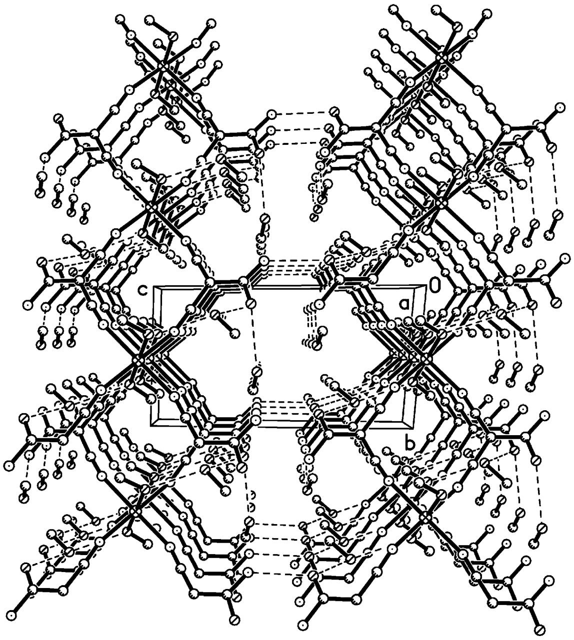

Fig. 2. Unit cell and the arrangement of 1D chains of **1** viewed from the *a* axis.

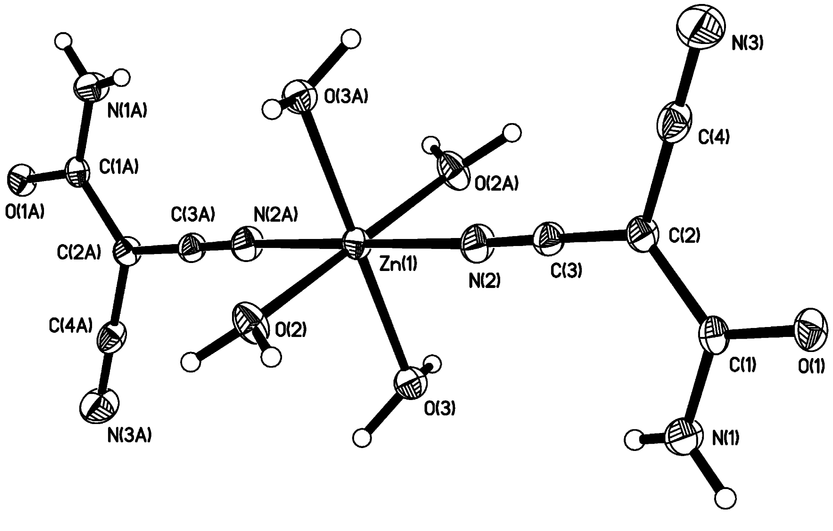

Fig. 3. The coordination diagram of $[Zn(cda)_2(H_2O)_4]\cdot 2H_2O$ (**2**) with atom numbering scheme.

coordination of Zn(II) and double $\mu_{1,5}$-*cda* bridging ligands. In the one-dimensional chain there exists a 12-membered ring which is constructed by two Zn(II) ions and double $\mu_{1,5}$-*cda* bridging ligands. Fig. 2 shows the unit cell and crystal packing viewed from the *a* direction. Hydrogen bonding interactions lead to a two-dimensional sheet in the *ab* plane, and these sheets stack along the *c* axis to form a three-dimensional crystal structure. The uncoordinated methanol molecules are trapped in the cavities, which are formed through the interaction of hydrogen bonding between the sheets.

3.2.2. [Zn(*cda*)$_2$(H$_2$O)$_4$]·2H$_2$O (**2**)

Fig. 3 shows the coordination diagram of **2** with the atom numbering scheme. It indicates that the Zn(II) ion is coordinated by two nitrogen atoms from nitrile groups and four aqua ligands. The coordination environment of the Zn(II) ion is a slightly distorted octahedron. The crystal structure of **2** is very similar to that of the complex [Ni(*cda*)$_2$(H$_2$O)$_4$]·2H$_2$O [20]. Fig. 4 shows the unit cell and the crystal packing viewed from the *b* direction. The coordination state of the complex is utterly different from the reported coordinated pattern of the Co(II) and the Ni(II) complexes that places the H$_2$O molecules in the outer sphere [18].

3.3. Fluorescent property

The fluorescence spectra for Na(*cda*) and the two complexes were measured at room temperature. For complex **1** the maximum absorption peak positions are at 362 nm in methanol solution and 328, 386 and 470 nm in the solid state, and the excited wavelength is selected at 362 nm both in methanol solution (9.5×10^{-3} mol·l^{-1}) and in the solid state. The maximum emission peaks are at 419 nm in methanol solution and 391 nm in the solid state. For complex **2** the maximum absorption

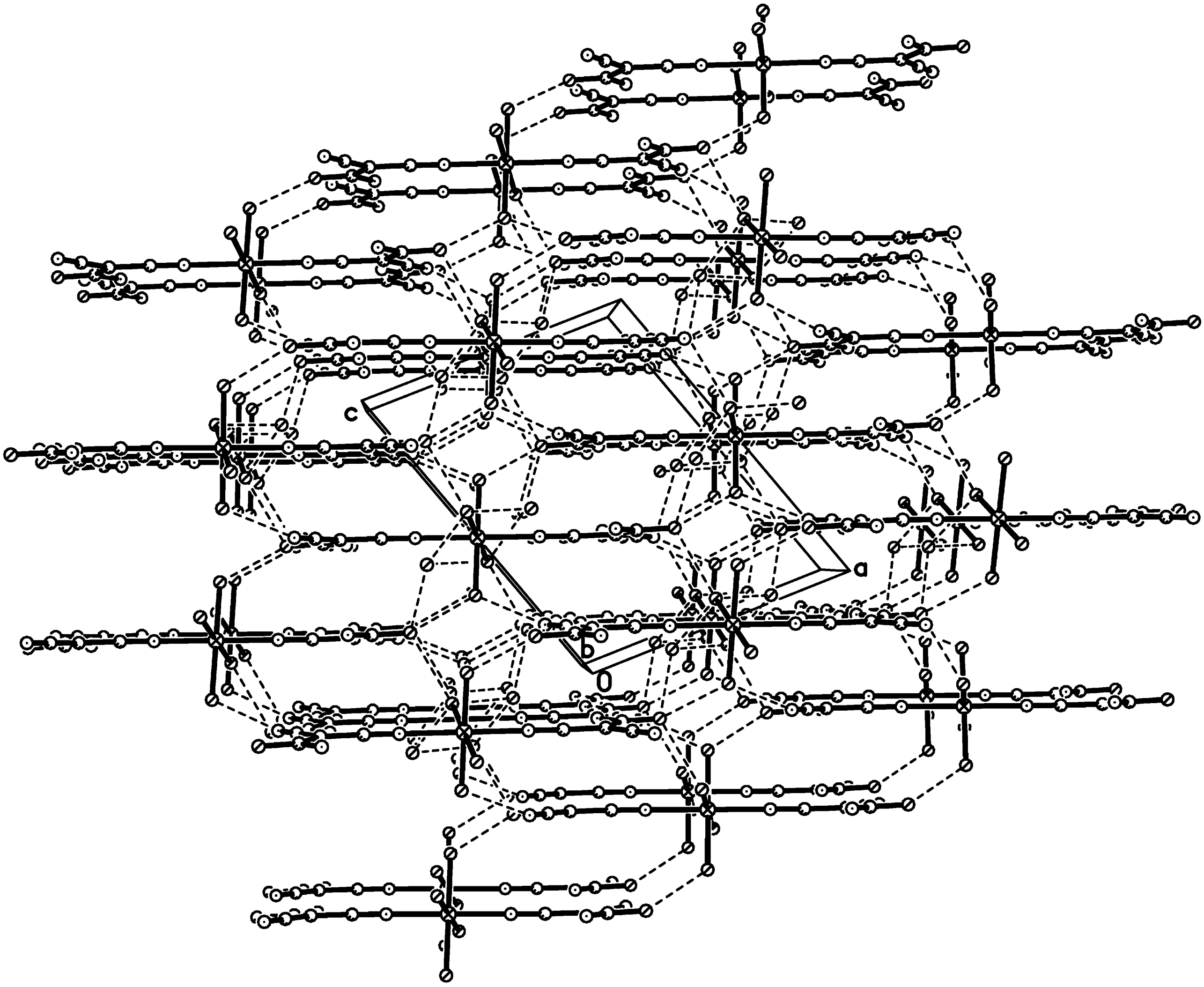

Fig. 4. Unit cell and the arrangement of the mononuclear complex (**2**) in the crystal.

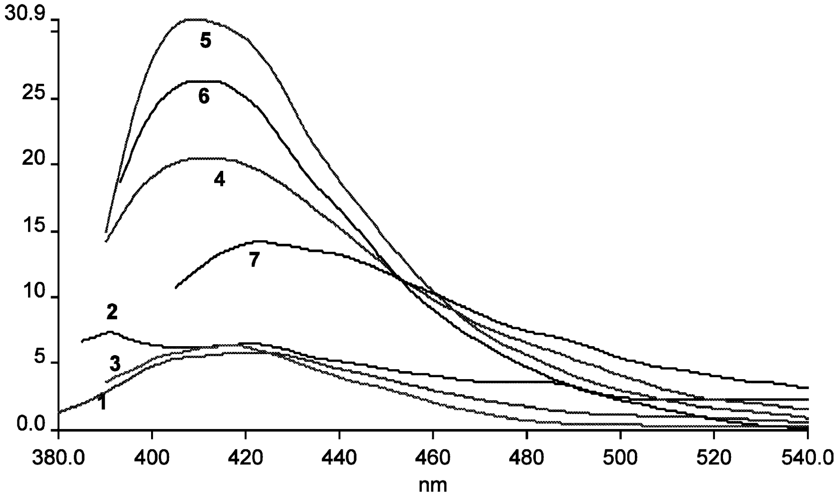

Fig. 5. The fluorescence spectra for Na(*cda*), $\{[Zn(cda)_2(CH_3OH)_2]\cdot 4CH_3OH\}_\infty$ (**1**) and $[Zn(cda)_2(H_2O)_4]\cdot 2H_2O$ (**2**) in solutions and in the solid state.

peak positions are at 324, 370 and 500 nm in H_2O solution and 324, 384 and 472 in the solid state, and the excited wavelength is selected at 370 nm both in H_2O solution (2.9×10^{-3} mol·l^{-1}) and in the solid state. The maximum emission peaks are at 415 nm in H_2O solution and 420 nm in the solid state. For Na(*cda*) the maximum absorption peak positions are at 380 nm in methanol solution, 370 nm in H_2O solution and 316, 388 and 470 nm in solid state, and the excited wavelengths are selected at 362 nm in methanol solution (1.6×10^{-3} mol·l^{-1}), 370 nm both in H_2O solution (7.7×10^{-3} mol·l^{-1}) and in the solid state. The maximum emission peaks are at 410 nm both in methanol solution and in H_2O solution, and 423 nm in the solid state. In Fig. 5 curves 1, 2, 3, 4, 5, 6 and 7 show the fluorescence spectra for complex **1** in methanol solution, complex **1** in the solid state, complex **2** in H_2O solution, complex **2** in the solid state, Na(*cda*) in methanol solution, Na(*cda*) in H_2O solution and Na(*cda*) in the solid state, respectively. Except curve 2, the fluorescence peak shapes are very similar and the peak positions are very close, which implies that the fluorescence emission of the complexes comes from *cda*. The chemical structures of organic fluorescence compounds [23–25] generally contain an aromatic ring, fused aromatic rings, or other conjugated ring systems along with fluorophores, such as >C=O, –N=O, –N=N–, >C=S, whereas *cda* does not possess a conjugated ring structure and it contains a fluorochromic group, –C≡N, which generally serves to decrease fluorescence intensity or quench fluorescence emission. In order to understand the fluorescence emission mechanism of *cda*, ab initio Cis/6-31G(d, p) calculations with the GAUSSIAN-94 program were conducted under the condition of the absence of a potential field around *cda*. The calculation results indicate that there is a rigid conjugated planar structure in *cda* both in the ground and excited state. The calculation results also indicate that there exists a transition peak at 458.80 nm assignable to a $\pi \rightarrow \pi^*$ transition and this may be the reason why *cda* exhibits fluorescence emission. Fig. 5 also indicates that the potential field around *cda* has a certain of influence on the maximum emission peak position and the emission intensity. The bathochromic shift of the maximum peak position for complex **1** in the solid state may arise from the different potential fields around *cda*.

4. Supplementary material

The X-ray crystallographic files, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 161866 and 161863 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, 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).

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References

[1] S.R. Batten, R. Robson, Angew. Chem., Int. Ed. Engl. 37 (1998) 1460.
[2] E.C. Constable, Prog. Inorg. Chem. 42 (1994) 67.

[3] J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, J.S. Miller, Science 252 (1991) 1415.
[4] W. Kaim, M. Moscherosch, Coord. Chem. Rev. 129 (1994) 157.
[5] K. Falk, M. Balanda, Z. Tomkowicz, F. Mascarenhas, J. Schilling, P. Klavins, W. Haase, Polyhedron 20 (2001) 1521.
[6] M. Mimalata, G.L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, T. Horino, Inorg. Chem. 37 (1998) 5651.
[7] F. Baumann, W. Kaim, J.A. Olabe, A.R. Parise, J. Jordanov, J. Chem. Soc., Dalton Trans. (1997) 4455.
[8] L. Ballester, A. Gutierrez, M.F. Perpinan, S. Rico, M.T. Azcondo, C. Bellitto, Inorg. Chem. 38 (1999) 4430.
[9] H. Hartmann, W. Kaim, I. Hartenbach, T. Schleid, M. Wanner, J. Fiedler, Angew. Chem., Int. Ed. 40 (2001) 2842.
[10] S.R. Batten, B.F. Hoskins, B. Moubaraki, K.S. Murray, R. Robson, J. Chem. Soc., Dalton Trans. (1999) 2977.
[11] S. Triki, F. Thetiot, J.S. Pala, S. Golhen, J.M. Clemente-Juan, C.J. Gomez-Garcia, E. Coronado, Chem. Commun. (2001) 2172.
[12] H. Hoshino, K. Iida, T. Kawamoto, T. Mori, Inorg. Chem. 38 (1999) 4229.
[13] A. Claramunt, A. Escuer, F.A. Mautner, N. Sanz, R. Vicente, J. Chem. Soc., Dalton Trans. (2000) 2627.
[14] G.A. Albada, M.E. Quiroz-Castro, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 298 (2000) 221.
[15] C. Kremer, C. Melian, J. Torres, M.P. Juanico, C. Lamas, H. Pezaroglo, E. Manta, H. Schumann, J. Pickardt, F. Girgsdies, O.N. Ventura, F. Lloret, Inorg. Chim. Acta 314 (2001) 83.
[16] S. Hunig, P. Erk, Adv. Mater. 3 (1991) 225.
[17] S.L. Bartley, K.R. Dunbar, Angew. Chem., Int. Ed. 30 (1991) 448.
[18] V.V. Skopenko, R.D. Lampeka, Ukr. Khim. Zh. 47 (1981) 1095.
[19] V.V. Skopenko, R.D. Lampeka, Ukr. Khim. Zh. 48 (1982) 1016.
[20] J.M. Shi, S.C. Zhu, L.D. Liu, W.T. Yu, H.L. Yin, J.L. Fan, Polish J. Chem. 75 (2001) 1591.
[21] J.M. Shi, W. Xu, Q.Y. Liu, F.L. Liu, Z.L. Huang, H. Lei, W.T. Yu, Q. Fang, Chem. Commun. (2002) 756.
[22] S. Trofimenko, E.L. Little, H.F. Mower, J. Org. Chem. (1962) 433.
[23] A.P. Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.
[24] H. Meier, Angew. Chem., Int. Ed. 40 (2001) 1851.
[25] J.V. Mello, N.S. Finney, Angew. Chem., Int. Ed. 40 (2001) 1536.