

Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstruc

A novel centrosymmetric dinuclear cadmium(II) Schiff base complex with unusual bridging carboxylate: Synthesis, crystal structure and luminescence properties

Shyamapada Shit^a, Joy Chakraborty^a, Brajagopal Samanta^a, Guillaume Pilet^b, Samiran Mitra^{a,*}

^a Department of Chemistry, Jadavpur University, Kolkata 700032, West Bengal, India

^b Groupe de Cristallographie et Ingénierie Moléculaire, Laboratoire des Multimatériaux et Interfaces, UMR 5615, Université Claude Bernard Lyon 1, Bât. Jules Roulin, 43 Bd du 11 Novembre 1918-69622. Villeurbanne Cedex. France

ARTICLE INFO

Article history: Received 12 September 2008 Accepted 2 October 2008 Available online 12 October 2008

Keywords: Dinuclear complex Schiff base Heptadentate Cd(II) Crystal structure Rare µ-2,2 carboxylato bridging Photoluminescence

ABSTRACT

A novel centrosymmetric dinuclear Cd(II) complex [CdL (CH₃COO)]₂ (**1**) has been synthesized by the reaction of Cd(CH₃COO)₂·2H₂O with a Schiff base ligand HL [HL = (*E*)-2-((pyridin-2-yl)methyleneamino)benzoic acid]. Title complex has been systematically characterized by elemental analysis, FT-IR, and thermal studies. Single crystal X-ray structural analysis reveals that Cd(II) centers in **1** adopt distorted monocapped octahedral geometry and held together by rare doubly μ -2, 2 carboxylato bridging which is believed to be first relating to anthranilic carboxylate. At room temperature, compound in the solid state exhibits moderate photoluminescence activities indicating its potential as promising photoactive material.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The rational design and synthesis of novel coordination complexes based on transition or non-transition metals and multifunctional bridging ligands is of great research interest, due to their interesting topologies and potential applications as functional materials. The most intelligent strategy to obtain coordination polymers is to employ appropriate bridging ligands that are capable of binding to several metal centers through direct bond formation. In this regard, Schiff base ligands have proven themselves very effective in constructing supramolecular architectures such as coordination polymers, double and triple helicates [1a,b] with their additional wide applications as antibacterial, antiviral, antifungal agents [2], in homogeneous or heterogeneous catalysis [3a-e] and magnetism [4]. Schiff bases are also considered as potential anticancer drugs [5a,b] and when administered as their metal complexes, the anticancer activity is enhanced in comparison to the free ligand [6a,b].

In this regard, Schiff base ligands with incorporated free carboxylate ends are also considered as useful because of their simultaneous activities as both chelator and a bridging ligand. Moreover the free carboxylate may take part in the charge neutralization of the target complex. Hence, the carboxylate group is one of the most widely used bridging ligands for designing polynuclear complexes having novel structural features. The versatility of this group as a ligand is illustrated by the variety of its coordination modes when acting as a bridge [7a,b]. Extensive work has been carried out by using multicarboxylate ligands because of their interesting structural characteristics [8a–f]. Several members of the aminopolycarboxylates/amino acids can also be referred in this regard.

In this context, anthranilic acid is considered as an important and competent precursor in the designing of carboxylate incorporated Schiff base ligands because of its free primary amine functionality which is useful during the condensation with an aldehyde/ketone while its free carboxylate end is considerably flexible from the point of view of the steric orientation in the formation of less strained covalent bonds with the metal centers, hence shows versatile bridging modes (Scheme 1a and b). Schiff bases derived from a large number of carbonyl compounds and amines or amino alcohols are plenty in the chemical literature, however, the studies on their optical properties, such as fluorescence, are not that much ample.

On the other hand, Cd(II) due to its d¹⁰ electronic configuration, is particularly suited for the construction of coordination polymers and networks. The spherical d¹⁰ configuration is associated with a flexible coordination environment so that geometries of these complexes can vary from tetrahedral to octahedral and severe distortions in the ideal polyhedron occur easily. Furthermore, due to the general lability of d¹⁰ metal ion complexes, the formation of coordination bonds is reversible which enables metal ions and li-

^{*} Corresponding author. Tel.: +91 033 2414 6666 x2505; fax: +91 033 2414 6414. *E-mail address:* smitra_2002@yahoo.com (S. Mitra).

^{0022-2860/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2008.10.002



Scheme 1. Bridging modes of anthranilic carboxylate in the deprotonated Schiff base ligand (HL).

gands to rearrange during the process of polymerization to give highly ordered network structures. Because of border-line acidity, cadmium(II) prefers to bind both hard and soft donors which thus widens its scope in the study of crystal engineering. Diamagnetic cadmium(II) is chosen for its d¹⁰ configuration, permitting a wide variety of geometries and coordination numbers. Cd(II) coordination polymers bear various topologies as the metal coordination number can be expanded up to seven and the directional property of the coordination bond is somewhat relaxed by the absence of any crystal field stabilization energy in the d¹⁰ electronic configuration. The terminal or blocking co-ligands, which are usually used along with the bridging ligand to complete the metal coordination sphere, can alter the supramolecular assembly and consequently the type of structure formed taking the advantage of the flexibility of the coordination sphere. Moreover, cadmium(II), though treated mainly as a toxic element to the biological systems, similar to Pb and Hg, has been found recently as the catalytic center in a newly discovered carbonic anhydrase [9]. It's complexes with nitrogen containing ligands are also used in ligand exchange chromatography [10]. Cadmium(II) Schiff base complexes are often found as photochemically important too.

Working on Schiff base transition metal complexes, our group has reported a few [10–14]. However, as a part of our continuing effort on the transition metal complexes with Schiff base ligands incorporating free carboxylate end [15–17], we have reported herein a novel centrosymmetric dinuclear cadmium(II) complex [CdL(CH₃COO)]₂ (1) [HL = (*E*)-2-((pyridin-2-yl)methyleneamino)benzoic acid]. Systematic characterization of the complex has been performed by elemental analysis, FT-IR, and thermal methods. Structural elucidation by the single crystal X-ray diffraction technique reveals that Cd(II) centers in 1 adopt distorted monocapped octahedron geometry and held together by rare μ -2,2 carboxylato bridging. Such bridging mode (Scheme 1c) is rare in the literature and is believed to be first relating to anthranilic carboxylate. Solid state photoluminescence measurement of 1 at room temperature indicates its potential to serve as photoactive material.

2. Experimental

2.1. Materials

All the chemicals and solvents used for the synthesis were of analytical grade. Pyridine-2-carboxaldehyde, $Cd(CH_3COO)_2 \cdot 2H_2O$, and anthranilic acid were purchased from Aldrich Chemical Co. Inc. and were used without any further purification. The solvents used were of analytical grade.

2.2. Syntheses of the ligand and complex

2.2.1. Synthesis of (E)-2-((pyridin-2-yl)methyleneamino)benzoic acid (HL)

The Schiff base HL was prepared following the literature procedure [18]. Pyridine-2-carboxaldehyde (0.535 g, 5 mmol) was refluxed with anthranilic acid (0.685 g, 5 mmol) in 50 ml methanol. A red solution was obtained. It was subjected to TLC which revealed the presence of some unreacted starting materials along with the Schiff base product. The Schiff base product was isolated by column chromatography in order to get it in the purified form. The purified ligand was then evaporated under reduced pressure to yield a gummy mass, which was dried and stored *in vacuo* over CaCl₂ for subsequent use. Yield: 1.061 g (87%). Anal. Calc. for C₁₃H₁₀N₂O₂: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.09; H, 4.43; N, 12.42%.

2.2.2. Synthesis of [CdL (CH₃COO)]₂ (1)

Appropriate quantity of the solid Schiff base ligand HL (0.452 g, 2 mmol) was dissolved in dry methanol (20 ml). A solution of $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.798 g, 3 mmol) in dry methanol (10 ml) was added to this solution. The mixture was stirred for 2 h at room temperature. The resulting yellow coloured solution was then filtered off and the filtrate was left undisturbed. After 10 days yellow hexagonal shaped X-ray diffraction quality single crystals separated out on the slow evaporation of the filtrate. They were filtered, and dried *in vacuo* over CaCl₂. Crystals are insoluble in common polar and non-polar solvents. Yield: 0.554 g (75%) with respect to the metal substrate. Anal. Calc. for C₃₀H₂₄Cd₂N₄O₈: C, 45.42; H, 3.05; N, 7.06. Found: C, 45.41; H, 3.02; N, 7.04 %.

2.3. Physical measurements

The Fourier transform infrared spectra of the ligand (HL) and **1** were recorded on a Perkin Elmer Spectrum RX I FT-IR spectrophotometer with a KBr disc in the range 4000–200 cm⁻¹. Elemental analyses (C, H, and N) were carried out using a Perkin Elmer 2400 II elemental analyzer. The emission spectra for both HL and **1** were recorded at room temperature (298 K) on a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric analyses were carried out at a heating rate of 10 °C/min with a Mettler-To-ledo star TGA/SDTA-851^e thermal analyzer system in a dynamic atmosphere of N₂ (flow rate 80 ml/min) in an alumina crucible for the range 25–630 °C.

2.4. Single crystal X-ray structure determination

A good diffraction quality air stable single crystal of **1** ($0.51 \times 0.88 \times 0.94$ mm) was mounted in a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Crystal data were collected using the software COLLECT [19a] at a temperature of 290 K. Cell refine-

Table 1

Crystallographic data collection and structural refinement for 1.

Chemical formula	C ₃₀ H ₂₄ Cd ₂ N ₄ O ₈	
Formula weight	793.34	
Crystal system	Monoclinic	
Space group	$P2_1/a$ (no.14)	
a (Å)	9.4019(2)	
b (Å)	17.6839(5)	
c (Å)	10.0512(3)	
α (°)	90	
β(°)	116.4890(10)	
γ (°)	90	
Ζ	2	
T (K)	290	
$\lambda_{Mo K\alpha}(Å)$	0.71073	
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.762	
$\mu ({\rm mm}^{-1})$	1.479	
F(000)	784	
θ Range (°)	2.3-28.8	
Total data	3984	
Unique data	3854	
Observed data $[I > 2\sigma(I)]$	2768	
N _{ref} ; N _{par}	2768; 199	
Final R Indices $[I > 2\sigma(I)]$	R1 = 0.0399, wR2 = 0.0492	
R indices (all data)	R1 = 0.0552, wR2 = 0.0610	
R _{int}	0.0399	
$\triangle \rho_{\rm max}$ (e Å ⁻³)	0.46	
$\rho_{\min} (e \text{ Å}^{-3}) -1.44$		
Goodness-of-fit on F^2	1.0587	

ments were carried out using DENZO-SCALEPACK [19a]. No significant intensity variation was observed for each of them. A total of 3984 reflections (3854 unique reflections, $R_{int} = 0.065$) were collected applying the boundary condition $I > 3\sigma(I)$. No absorption correction was applied to the data sets of 1. Data reduction was performed using DENZO-SCALEPACK for 1 [19a]. According to the observed systematic extinctions, the structure of 1 was solved by direct methods using the SIR97 [19b] program combined with Fourier difference syntheses and refined against F using reflections maintaining the boundary condition $I > 3\sigma(I)$ (CRYSTALS program) [19c]. The molecular graphics and crystallographic illustrations of the complex were prepared using the CAMERON [19d], ORTEP [19e] programs. For all non-hydrogen atoms, the anisotropic displacement parameters have been refined successfully. Hydrogen atoms of the aromatic rings and the imino groups were placed geometrically and refined as a riding model taken from a Fourier difference map and refined with isotropic thermal parameters. Maximum, minimum peaks $(e^{A^{-3}})$ in the final difference Fourier synthesis were found as 0.46, and -1.44, respectively. All the relevant crystallographic data and structure refinement parameters for 1 are summarised in Table 1.

3. Results and discussion

3.1. Fourier transform infrared spectra

The solid state Fourier transform infrared spectra of HL and **1** were recorded on a Perkin Elmer Spectrum RX I FT-IR spectrophotometer in the range 4000–200 cm⁻¹. The samples were studied as powder dispersed in KBr pellets. HL displayed a sharp strong peak at 1642 cm⁻¹ corresponds to imine (CH=N) group. HL also showed two bands at 1605 and 1413 cm⁻¹ assignable to $v_{as}(COO^-)$ and $v_s(COO^-)$, respectively, for free carboxylate. The ligand (HL) shows strong sharp bands at 1586, 1473 and 1430 cm⁻¹ correspond to the pyridine skeleton [20].

However, the azomethine stretching frequency is lowered by 30 cm^{-1} upon complexation, indicating the coordination of imine (CH=N) nitrogen, which is further supported by bands in the range of 455 cm⁻¹ corresponding to v(Cd–N) observed for **1**. Bands

observed at 1412 and 1545 cm⁻¹ in the complex may be assigned for $v_s(COO^-)$ and $v_{as}(COO^-)$ vibrations. The difference of these two frequencies [$\Delta v = v_s(COO^-) - v_{as}(COO^-)$], 133 cm⁻¹ indicates the bridging coordination modes of the carboxylate group of the Schiff base [20,21]. Sharp band appearing at 375 cm⁻¹ corresponds to v(Cd—O) is also observed for **1** [14]. Observed strong sharp bands in the regions 1605–1597, 1485–1460, 1445–1420, 1055–1040 and 1015–1005 cm⁻¹ for **1** may be correlated to the coordinated pyridine ring [20].

3.2. Crystal structure of [CdL (CH₃COO)]₂ (1)

Single crystal X-ray structure analysis shows that the structure of 1 consists of a discrete dimeric unit. An ORTEP view of the asymmetric unit of the complex has been shown in the Fig. 1. Structure determination reveals the centrosymmetric nature of the dimer in which the coordination environments of metal atoms are altogether satisfied by deprotonated Schiff base ligands and acetate ions. The Cd(II) ions in the complex are hepta coordinated. Five coordinating positions of each Cd(II) center is satisfied by five donor atoms from two Schiff base ligands and the other two coordinating positions are satisfied by the chelating acetate ion. The coordination geometry of cadmium atoms [Cd1 and its symmetry related counterpart] can be best described as a distorted monocapped octahedron. A pyridine nitrogen N6 and an imine nitrogen N7 along with five oxygen donors (O4 and O5, coming from chelating acetate whereas O2 and O3, from a chelating anthranilic carboxylate of the same Schiff base ligand, remaining oxygen atom O2* is a symmetry related counterpart of O2 coming from another Schiff base ligand) constitute the N₂O₅ donor set around the Cd(II) metal center [Cd1-N6, 2.366(4); Cd1-N7, 2.366(3); Cd1-O2, 2.412(3); Cd1-O2*, 2.379(3); Cd1-O3, 2.426(3); Cd1-O4, 2.299(3) and Cd1-O5, 2.391(4) Å (translation of symmetry codes to equivalent positions: * = 1 - x, -y, -z)]. The carboxylate group of acetate ligand acts as a bidentate chelating group while the free anthralinic carboxylate end of the Schiff base acts as bridging as well as chelating groups (totally tridentate) in a μ -2.2 mode, where two oxygen atoms of the carboxylate group of two bridging anthranilic carboxylate chelate and also bridge the two adjacent Cd(II) centers, thus yielding a four-membered {Cd-O-C-O}₂ metallacycle [22] with a Cd....Cd separation of 3.902(3) Å. Thus two adjacent cadmium centers are connected to each other by a doubly oxobridging mode of this carboxylate through the atoms O2 and



Fig. 1. ORTEP view of the dimeric unit of **1**, with atom labels. Displacement ellipsoids are shown at 50% probability level. The hydrogen atoms are omitted for clarity (translation of symmetry codes to equivalent positions: * = 1 - x, -y, -z).

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

Bond lengths	(Å)	Bond angles	(°)
Cd1-02	2.412(3)	02-Cd1-04	146.56(11)
Cd1-04	2.299(3)	02-Cd1-05	92.45(9)
Cd1-05	2.391(4)	02-Cd1-N6	108.33(11)
Cd1—N6	2.366(4)	02-Cd1-N7	67.55(10)
Cd1—N7	2.366(3)	02-Cd1-02*	70.90(9)
Cd1-02*	2.379(3)	02-Cd1-03*	104.66(10)
Cd1-03*	2.246(3)	04–Cd1–O5	55.26(10)
_		04-Cd1-N6	102.50(13)
_	-	04-Cd1-N7	113.02(11)
_	-	02*-Cd104	97.77(11)
_	-	03*-Cd104	92.06(11)
_	-	05-Cd1-N6	137.40(12)
_	-	05-Cd1-N7	85.55(12)
-	-	02*-Cd105	89.55(11)
_	-	03*-Cd105	129.13(13)
_	-	N6-Cd1-N7	69.87(12)
-	-	02*-Cd1N6	131.97(10)
-	-	O3*-Cd1N6	81.90(13)
-	-	02*-Cd1N7	137.87(10)
-	-	O3*-Cd1N7	145.29(13)
_	-	02*-Cd103*	54.10(11)
-	-	Cd1-02-C10	119.2(2)
-	-	Cd1-02-Cd1*	109.10(11)
-	-	Cd1*-02-C10	93.3(2)
-	-	Cd1*-03-C10	91.3(2)
_	-	Cd1-04-C11	93.9(2)
_	-	Cd1-05-C11	89.9(3)
_	-	Cd1-N6-C14	125.7(3)
-	-	Cd1-N6-C15	116.6(3)
-	-	Cd1-N7-C9	122.4(3)
-	-	Cd1-N7-C19	117.0(3)

Translation of symmetry codes to equivalent positions: * = 1 - x, -y, -z.

O2*. Such bridging modes exhibited by the single anthranilic carboxylate is almost rare in the chemical literature of the related systems and believed to be first of its own kind. The relevant bond distances and angles are summarized in Table 2.

3.3. Thermogravimetric analysis

Thermogravimetric analysis of the complex reveals that it is thermally stable up to 160 °C after which it undergoes decomposition in two steps. A total mass loss of 14.50% corresponds to the release of two chelating acetate ions per formula unit observed between 161 and 230 °C in the TGA curve. Another mass loss takes place between 231 and 605 °C corresponds to the release of two Schiff base ligands indicated by a total mass loss of 64%.

3.4. Photoluminescence properties

The emission spectra of HL and **1** in their solid state were recorded at room temperature. The luminescence spectra of both HL and **1** are depicted in Fig. 2. It is noteworthy that HL shows a broad blue-fluorescent emission around 520 nm upon excitation at 435 nm [Fig. 2: *solid brown line*¹] while complex **1** exhibits a very strong blue-shifted fluorescent emission around 465 nm upon excitation at 380 nm [Fig. 2: *solid blue line*]. Therefore, the emission of **1** may not be assigned to intraligand fluorescent emission but be attributed to ligand-to-metal charge transfer (LMCT) [23–26]. In comparison HL molecule, **1** displays intense luminescence, undoubtedly owing to the chelating of the ligand to the metal center. This enhances the "rigidity" of the ligand and thus reduces the loss of



Fig. 2. Luminescence spectra of HL and complex **1** (λ_{exc} = 435 nm for HL and 380 nm for **1**).

energy through radiationless decay of the intraligand emission excited state [27,28].

As a result, the reported complex may be regarded as an excellent candidate of violet-blue light emitting materials, since the condensed material is highly thermally stable and insoluble in common polar and non-polar solvents [24,26]. Enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical applications of these complexes. Factors like a simple binding of ligand to the d¹⁰ metal ions [29], an increased rigidity in structure of the complexes [30], a restriction in the photoinduced electron transfer (PET) [31], etc. may be assigned for the increase in the photoluminescence.

4. Conclusion

In this paper we have reported a novel centrosymmetric dinuclear cadmium(II) complex with a Schiff base ligand incorporating free carboxylate end. Systematic characterizations of the complex by elemental analysis, FT-IR, and thermal methods have also been discussed. X-ray structural analysis reveals that each Cd(II) center in **1** adopts distorted monocapped octahedral geometry and held together by doubly μ -2,2 bridging anthranilic carboxylates which is rare in literature and believed to be first relating to anthranilic carboxylate. Solid state photoluminescence measurement at room temperature indicates its potential to serve as photoactive material.

5. Supplementary data

X-ray crystallographic data in the 'CIF' format corresponding to the complex reported in this paper has been deposited with the Cambridge Crystallographic Data Center and supplementary crystallographic data for this paper can be obtained free of charge on request at http://www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk], quoting the CCDC number 636956 for **1**.

Acknowledgements

Joy Chakraborty is grateful to the University Grants Commission, New Delhi, Government of India for the award of a Senior Research Fellowship to him. The financial assistance from AICTE, New Delhi, Government of India is also gratefully acknowledged.

¹ For interpretation of the references to color in this figure, the reader is referred to the web version of this article.

References

- [1] [a] R. Ziessel, Coord. Chem. Rev. 216 (2001) 195;
- [b] M. Albrecht, Chem. Rev. 101 (2001) 3457.
- S. Chandra, X. Sangeetika, Spectrochim. Acta A 60 (2004) 147.
- [3] [a] E. Fujita, B.S. Brunschwig, T. Ogata, S. Yanagida, Coord. Chem. Rev. 132 (1994) 195;
 - [b] E. Kimura, S. Wada, M. Shiyonoya, Y. Okazaki, Inorg. Chem. 33 (1994) 770;
 - [c] B. De Clercq, F. Verpoort, Macromolecules 35 (2002) 8943: [d] T. Opstal, F. Verpoort, Angew. Chem. Int. Ed. Engl. 42 (2003) 2876;
 - [e] B. De Clercq, F. Lefebvre, F. Verpoort, Appl. Catal. A 247 (2003) 345.
- [4] S.L. Lambert, C.L. Spiro, R.R. Gagne, D.N. Hendriekson, Inorg. Chem. 21 (1982) 68.
- [5] [a] D. Kessel, A.F.A. Sayyab, E.M.H. Jaffar, A.H.H.A. Lanil, Iraqi J. Sci. 22 (1981) 312:
- [b] E.M. Hodnett, W.J. Dunn, J. Med. Chem. 13 (1970) 768.
- [6] [a] E.M. Hodnett, W.J. Dunn, J. Med. Chem. 15 (1970) 765.
 [6] [a] E.M. Hodnett, W.J. Dunn, J. Med. Chem. 15 (1972) 339;
 [b] J. Chakraborty, R.N. Patel, J. Indian Chem. Soc. 73 (1996) 191.
- [7] [a] M. Kato, Y. Muto, Coord. Chem. Rev. 92 (1988) 45; [b] C. Oldham, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987.
- [a] J.J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko, Angew. Chem. Int. Ed. Engl. 40 (2001) 2113:
 - [b] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O_Keeffe, O.M. Yaghi. Science 300 (2003) 1127;
 - [c] S. M. -F. Lo, S. S.-Y. Chui, L.Y. Shek, Z.Y. Lin, X.X. Zhang, G.H. Wen, I.D. Williams, J. Am. Chem. Soc. 122 (2000) 6293;
 - [d] F. Millange, C. Serre, G. Frey, Chem. Commun. 4 (2002) 822;
 - [e] X.M. Chen, G.F. Liu, Chem. Eur. J. 8 (2002) 4811;
 - [f] J.H. Luo, M.C. Hong, R.H. Wang, R. Cao, L. Han, D.Q. Yuan, Z.Z. Lin, Y.F. Zhou, Inorg, Chem. 42 (2003) 4486.
- [9] T.W. Lane, F.M.M. Morel, Proc. Natl. Acad. Sci. USA 97 (2000) 4627.
- [10] R. Karmakar, C.R. Choudhury, D.L. Hughes, S. Mitra, Inorg. Chim. Acta 360 (2007) 2631, and references therein.
- [11] C.R. Choudhury, S.K. Dey, N. Mondal, S. Mitra, S.O.G. Mahalli, K.M.A. Malik, J. Chem. Crystallogr. 31 (2002) 57. [12]
- [a] C.R. Choudhury, S.K. Dey, S. Mitra, N. Mondal, J. Ribas, K.M.A. Malik, Bull. Chem. Soc. Jpn. 77 (2004) 959;
 - [b] R. Karmakar, C.R. Choudhury, G. Bravic, J.-P. Sutter, S. Mitra, Polyhedron 23 (2004) 949;
 - [c] S.K. Dey, N. Mondal, M.S. El Fallah, R. Vicente, A. Escuer, X. Solans, M.F. Bardia, T. Matsushita, V. Gramlich, S. Mitra, Inorg. Chem. 43 (2004) 2427; [d] P. Talukder, A. Datta, S. Mitra, G. Rosair, M.S. El Fallah, J. Ribas, Dalton Trans. (2004) 4161.
- [13] [a] C.R. Choudhury, S.K. Dey, R. Karmakar, C. De Wu, C.-Z. Lu, M.S. El Fallah, S. Mitra, New J. Chem. 2 (2003) 1360;

- [b] M.K. Saha, D.K. Dev, B. Samanta, A.I. Edwards, W. Clegg, S. Mitra, Dalton Trans. (2003) 488
- [c] N. Mondal, M.K. Saha, B. Bag, S. Mitra, G. Rosair, M.S. El Fallah, Polyhedron 20 (2001) 579:
- [d] N. Mondal, S. Mitra, V. Gramlich, S.O.G. Mahalli, K.M.A. Malik, Polyhedron 20 (2001) 135.
- [14] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, Polyhedron 25 (2006) 1753.
- [15] C.R. Choudhury, A. Datta, V. Gramlich, G.M.G. Hossain, K.M.A. Malik, S. Mitra, Inorg. Chem. Commun. 6 (2003) 790.
- [16] S.K. Dey, B. Bag, K.M.A. Malik, M.S. El Fallah, J. Ribas, S. Mitra, Inorg. Chem. 42 (2003) 4029.
- S. Sen, S. Mitra, D. Luneau, M.S. El Fallah, J. Ribas, Polyhedron 25 (2006) 2737. [18] R. Shukla, P.K. Bhardwaj, J.V. Hall, H. Whitmire, Polyhedron 13 (1994) 2391.
- and the references therein. [19] [a] Nonius COLLECT, DENZO, SCALEPACK, SORTAV: KappaCCD Program US B.V.,
- Delft, The Netherlands, 1999.; [b] G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, D. Siliqi, M.C. Burla, G. Polidori, M. Camalli, Acta Crystallogr. A52 (1996) C-79; [c] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, Crystals, issue 11, Chemical Crystallography Laboratory, Oxford, UK, 1999.; [d] L.J. Farrugia, WinGX, J. Appl. Crystallogr. 32 (1999) 837;
- [e] L.J. Farrugia, Ortep-3 for Windows, J. Appl. Crystallogr. 30 (1997) 565. [20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination
- Compounds, fifth ed., John Wiley, New York, 1997 (Part A and B). C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S.P. [21] Perlepes, Polyhedron 23 (2004) 83.
- [22] G. Mahmoudi, A. Morsali, A.D. Hunter, M. Zeller, Inorg. Chim. Acta 360 (2007) 3196.
- [23] J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, X.M. Chen, Inorg. Chem. 40 (2001) 6328.
- [24] X.L. Wang, C. Qin, E.B. Wang, Y.G. Li, N. Hao, C.W. Hu, L. Xu, Inorg. Chem. 43 (2004) 1850.
- [25] J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Hu, W.X. Du, L.M. Wu, H.H. Zhang, R.Q. Sun, Inorg. Chem. 41 (2002) 1391.
- [26] J. Tao, M.L. Tong, J.X. Shi, X.M. Chen, S.W. Ng, Chem. Commun. (2000) 2043
- [27] S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong, Inorg. Chem. 43 (2004) 830
- [28] L.Y. Zhang, G.F. Liu, S.L. Zheng, B.H. Ye, X.M. Zhang, X.M. Chen, Eur. J. Inorg. Chem. (2003) 2965.
- [29] P. Purkayastha, G.K. Patra, D. Datta, N. Chattopadhyay, Indian J. Chem. A 39 (2000) 375.
- [30] L.-Z. Cai, W.-T. Chen, M.-S. Wang, G.-C. Guo, J.-S. Huang, Inorg. Chem. Commun. 7 (2004) 611.
- G. Hennrich, H. Sonnenschein, U.R. Genger, J. Am. Chem. Soc. 121 (1999) [31] 5073.