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Synthesis, structure and luminescence behaviour of bis(tridentate) Schiff base bridged dinuclear lead(II) pseudohalides

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1. Introduction

ABSTRACT

Two pentacoordinated dinuclear lead(II) compounds $[Pb_2(pbap)(N_3)_4]$ (1) and $[Pb_2(pbap)(NCS)_4]$ (2) $[pbap = N-((1-pyridin-2-yl)benzylidene)-N'-[2-(4-{2-[((1-pyridin-2-yl)benzylidene)amino]ethyl}pipera-zin-1-yl)ethyl]amine] are prepared and characterized using microanalytical, spectroscopic, thermal and other physicochemical results. Single crystal X-ray diffraction measurements have been made to define the metal coordination spheres. Structural analyses reveal dinucleating bis(tridentate) behaviour of the hexadentate Schiff base (pbap) binding two metal ions. In the centrosymmetric dimers 1 and 2, each lea-d(II) center adopts a distorted square pyramidal geometry with PbN₅ chromophore ligated by each (N^p, Nⁱ, N^a) donor set of pbap and two N atoms of terminal pseudohalides. In DMF solutions at room temperature the complexes display high-energy intraligand <math>{}^1(\pi-\pi)$ fluorescence.

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The study of mono-, di- and polynuclear complexes of lead(II) is an important objective because of their interesting synthetic, structural, spectroscopic and optoelectronic features [1–4]. The essential prerequisites for such research are the judicious choice [5] of organic spacers and inorganic/organic terminals/bridges that may lead to directed properties. Recently, we are interested [6-8] in the construction of different coordination molecules through variation of ligand backbones and metal ion coordination environments; in this regard, Schiff base spacers and pseudohalide terminals/bridges have been used. Schiff bases [9] are recently focused by the coordination chemists as versatile organic ligands because of their preparative accessibilities, structural varieties, varied denticities and subtle steric and/or electronic control on their frameworks. Pseudohalides like homoatomic azide and heteroatomic thiocyanate [10] can bind metal ions with their different bonding modes [6-8,11-14] affording a good number of mono-, di- and polymeric com-

pounds in concert with organic ligands of varied denticities. The present work stems from our interest to examine the coordination behaviour a hexadentate Schiff base, [*N*-((1-pyridin-2-yl)benzyli-

dene)-N'-[2-(4-{2-[((1-pyridin-2-yl)benzylidene)amino]ethyl}piperazin-1-yl)ethyl]amine] (pbap) towards lead(II) in combination with two pseudohalides viz. azide and thiocyanate, that remains unexplored todate. Successfully, we have synthesized and X-ray crystallographically characterized two dinuclear compounds, $[Pb_2(pbap)(N_3)_4]$ (1) and $[Pb_2(pbap)(NCS)_4]$ (2), where pbap shows bis(tridentate) coordination motif assembling two lead(II) centers and the pseudohalides remain as terminals. The details of syntheses, structures, and thermal and luminescence behaviours of these compounds are described here.

2. Experimental

2.1. General remarks and physical measurements

2.1.1. Materials

High purity 2-benzoylpyridine (Lancaster, UK), 2-[4-(2-aminoethyl)-piperazin-1-yl]ethylamine (Aldrich, USA), sodium azide (E. Merck, India), ammonium thiocyanate (E. Merck, India) and lead(II) acetate (E. Merck, India) were purchased from respective concerns and used as received. All other chemicals and solvents were AR grade and were used as received. The Schiff base (pbap) was prepared following a reported method [15] described elsewhere. The synthetic reactions and work-up were done in open air.

Caution! Azido compounds of metal ions are potentially explosive [16] especially in the presence of organic ligands. Only a small



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amount of these materials should be prepared and handled with care.

2.1.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm⁻¹) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Thermal behaviour was investigated with a Perkin-Elmer Diamond TG/DT analyzer heated from 30-750 °C under nitrogen. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution and dry DMF was used as solvent. Ground state absorption (in CH₂Cl₂, CH₃OH and DMF) and steady-state fluorescence measurements (in dry DMF) were made with a Jasco model V-530 UV-vis spectrophotometer and Hitachi model F-4500 spectrofluorimeter, respectively. Timeresolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer Edinburgh Instruments, model 199; a hydrogen filled coaxial flash lamp with a pulse width of 1.2 ns at FWHM and a Philips XP-2020Q photomultiplier tube were used as the excitation source and the fluorescence detector.

2.2. General synthesis of the complexes

2.2.1. $[Pb_2(pbap)(N_3)_4]$ (1) and $[Pb_2(pbap)(NCS)_4]$ (2)

A methanolic solution (5 mL) of pbap (0.503 g, 1 mmol) was added dropwise to a solution of Pb(OAc)₂.3H₂O (0.758 g, 2 mmol) in the same solvent (10 mL) followed by NaN_3 (0.260 g, 4 mmol) in MeOH (50 mL). The yellow solution was filtered and the supernatant liquid was kept in air for slow evaporation. After a few days single crystals of 1 that separated, were filtered, washed with toluene and dried in vacuo over silica gel indicator. Yield: 0.815 g (75%). 2 was prepared using a similar procedure and reaction stoichiometry as described in **1** except that NH₄SCN (0.304 g, 4 mmol) instead of NaN₃ was used. Yield: 0.804 g (70%). Anal. Calc. For C₃₂H₃₄N₁₈Pb₂ (1): C, 35.38; H, 3.15; N, 23.31; Found: C, 35.29; H. 3.18; N, 23.39%. IR (KBr, cm^{-1}): v(N=N=N) 2019, 2000; v(C=N) + v(C=C) 1618, 1592. Λ_M (DMF, Ω^{-1} cm² mol⁻¹): 5. UVvis (λ , nm): 272. Anal. Calc. For C₃₆H₃₄N₁₀S₄Pb₂ (**2**): C, 37.60; H, 2.98; N, 12.23; Found: C, 37.69; H, 2.93; N, 12.28%. IR (KBr, cm^{-1}): v(N=C=S) 2036, 2020; v(C=N) + v(C=C) 1626, 1592; v(C-C)S) 768. Λ_{M} (DMF, Ω^{-1} cm² mol⁻¹): 4. UV–vis (λ , nm): 273.

2.3. X-ray crystallographic study

Single crystals of 1 and 2 suitable for X-ray analyses were selected from those obtained by slow evaporation of methanolic solutions of the reaction mixtures at 298 K. Diffraction data were collected at 293(2) K on a Bruker SMART APEX-II CCD area-detector diffractometer using graphite monochromated Mo-K α radiation $(\lambda = 0.71073 \text{ Å})$. The unit cell parameters were obtained from SAINT; absorption corrections were performed with SADABS [17]. A summary of the crystallographic data and structure determinant parameters is given in Table 1. Of 12,029 (1) and 13,907 (2) collected reflections, 2103 (1) and 4515 (2) unique reflections were recorded using the ω scan technique. The structures were solved by direct methods using SHELXS-97 [18]. All hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier maps, the residual maximum and minimum were 0.938 and $-0.793 \text{ e}\text{\AA}^{-3}$ (for **1**) and 3.702 and $-1.901 \text{ e}\text{\AA}^{-3}$ (for 2). All calculations were carried out using PLATON [19] and ORTEP-32 [20].

Table 1

Compounds	1	2
Formula	C ₃₂ H ₃₄ N ₁₈ Pb ₂	C ₃₆ H ₃₄ N ₁₀ S ₄ Pb ₂
Weight	1086.21	1149.97
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	C2/c
a/Å	16.1597(12)	27.517(5)
b/Å	8.0973(6)	10.674(2)
c/Å	15.3779(12)	13.075(2)
α°	90.00	90.00
β°	110.982(2)	100.837(3)
γ°	90.00	90.00
V/Å ³	1878.8(2)	3771.8(12)
λ/Å	0.71073	0.71073
$ ho_{ m calcd}/ m g~cm^{-3}$	5.175	2.024
Z	2	4
T/K	293(2)	293(2)
μ (mm ⁻¹)	55.797	9.180
F(000)	2400	2192
θ ranges (°)	1.35 to 21.30	1.51 to 28.38
h/k/l	-16, 16/-8, 8/-15,	-34, 36/-14, 14/
	15	-5,17
Reflections collected	12,029	13,907
Independent reflections	2103	4515
Data/restraints/parameters	2103/0/235	4515/0/235
Goodness-of-fit on F^2	0.779	1.032
Final R indices $[I > 2\sigma(I)]$	R = 0.0344,	R = 0.0328,
	wR = 0.0924	wR = 0.0800
R indices (all data)	R = 0.0533,	R = 0.0446,
	wR = 0.1105	wR = 0.0843
Largest peak and hole (eÅ ⁻³)	0.938 and -0.793	3.702 and -1.901

Weighting scheme: $R = \Sigma ||F_0| - |F_c||/\Sigma ||F_0|$, $wR = [\Sigma w (F_0^2 - F_c^2) 2/\Sigma w (F_0^2)^2]^{1/2}$. Calc. $w = 1/[\sigma^2 (F_0^2) + (0.1000P)^2 + 0.5611P]$ (1). Calc. $w = 1/[\sigma^2 (F_0^2) + (0.0487P)^2 + 1.8739P]$ (2); where $P = (F_0^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. Synthesis and formulation

The pentacoordinated dinuclear compounds 1 and 2 initially formed in methanolic solutions at room temperature containing a 1:1:2 mixture of Pb(OAc)₂·3H₂O, pbap and NaN₃ or NH₄NCS as is the case - a reactant ratio used to isolate octacoordinated mononuclear lead(II) compounds of the composition $[Pb(pbap)(X)_2]$ (X=N₃⁻, NCS⁻). However, microanalyses showed a 2:1:4 ratio of metal, blocking ligand and pseudohalides. Reactant ratios corresponding to the product stoichiometry afforded better yields of 1 and 2. The compounds were characterized using microanalyses (C, H and N), solution electrical conductivity measurements, spectroscopic and thermal investigations. The microanalytical data are in good agreement with the proposed formulas. The air-stable complexes are soluble in a range of common organic solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide and dimethylsulphoxide, but are insoluble in water. In DMF solutions, 1 and 2 behave as non-electrolytes as reflected in their low conductivity values ($\sim 5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) [21]. In IR, $v_{as}(X)$ stretches appear as strong bands at 2019 and 2000 cm⁻¹ in 1 and at 2036 and 2020 cm⁻¹ in 2 indicating the existence of different force constants of the pseudohalides in each compound. The positions of bands are in line with terminal nature of the pseudohalides in **1** and **2** and N-coordination of the thiocyanates [11] in **2**. A band corresponding to the v(C-S) stretching frequency appears at 768 cm⁻¹ in **2**. The Schiff base, pbap, in the metal bound states exhibit v_{as}(C=N) plus v_{as}(C=C) stretching vibrations [22] at \sim 1620 and \sim 1590 cm⁻¹. All other characteristic organic ligand vibrations are seen in the range 1600–600 cm⁻¹. Light yellow solutions of 1 and 2 in CH₂Cl₂/MeOH/DMF exhibit strong absorptions at



Fig. 1. ORTEP representation of [Pb₂(pbap)(N₃)₄] (1) with atom numbering scheme and 20% probability ellipsoids for all non-hydrogen atoms.

272 and 273 nm, respectively due to ligand based transition [23]. The solvent-independent spectral behaviour is presumably due to $\pi - \pi^*$ transition.

3.2. Description of the crystal structures of $[Pb_2(pbap)(N_3)_4]$ (1) and $[Pb_2(pbap)(NCS)_4]$ (2)

Structural analyses reveal that crystal lattices of **1** and **2** consist of dinuclear neutral $[Pb_2(pbap)(N_3)_4]$ and $[Pb_2(pbap)(NCS)_4]$ units. ORTEP diagrams with atom numbering schemes of **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond distances and bond angles relevant to the metal coordination spheres are set in Tables 2 and 3.

The tailored hexadentate Schiff base (pbap) belongs to a symmetrical N^p , N^i , N^a , N^a , N^p type, where N^p , N^i and N^a are N(pyridine), N(imine) and N(amine) donor centers, respectively. The dinucleating bis(tridentate) view of pbap and two pairs of donor (N^p , N^i , N^a) set arrangements through incorporation of the ring within the bridge in **1** and **2** is evident in Figs. 1 and 2. The Schiff base (pbap) is placed in a crystallographic inversion center in both

1 and 2. The coordination polyhedron around each pentacoordinated lead(II) center is best described as a distorted square pyramid as exemplified by its tau parameter (τ = 0.362 in **1** and τ = 0.290 in **2**) [24] with PbN₅ chromophore. The distortion from ideal square pyramidal geometry is due to asymmetric nature of the Schiff base and deviations of the refine angles (90°/180°) formed at the metal center. In the centrosymmetric dimers, two lead(II) centers (Pb1/ Pb1a in 1 and Pb/Pba in 2) are bound by bis(tridentate) behaviour of pbap through donation of one N^p (N4/N4a in **1** and N1/N1a in **2**), one Nⁱ (N5/N5a in 1 and N2/N2a in 2) and one N^a (N16/N16a in 1 and N3/N3a in 2) atoms to each metal; fourth and fifth coordination sites are occupied with two terminal N atoms (N6/N6a and N7/N7a in 1 and N1A/N1Aa and N1B/N1Bb in 2) of the pseudohalides. The intramolecular Pb...Pb distances are 6.8125(7) Å in 1 and 6.8659(11) Å in 2. The basal dimeric plane consists of four N (N^p, N^a) atoms of pbap along with four terminal azide N atoms in 1 and four terminal thiocyanate N atoms in 2, while the apical position of each lead(II) center is occupied by Nⁱ atoms of pbap. Each lead(II) center deviates (0.764 Å in 1 and 0.830 Å in 2) opposite to the apical pseudohalide from the mean basal plane. Pb-N(basal)



Fig. 2. Molecular structure of [Pb₂(pbap)(NCS)₄] (2); (ORTEP, 20% ellipsoids).

Table 2	
Selected bond distances (Å) and bond angles (°) for 1.	
Bond distances	

Dona aistances			
Pb(1)-N(4	2.501(9)	N(6)-N(8)	1.18(2)
Pb(1)-N(5)	2.435(10)	N(8)-N(9)	1.17(2)
Pb(1)-N(6)	2.619(12)	N(7)-N(11)	1.199(16)
Pb(1)-N(7)	2.475(11)	N(11)-N(10)	1.165(17)
Pb(1)-N(16)	2.682(11)		
Bond angles			
N(6)-Pb(1)-N(4)	81.3(4)	N(4)-Pb(1)-N(7)	83.6(3)
N(6)-Pb(1)-N(5)	77.8(4)	N(4)-Pb(1)-N(16)	133.7(3)
N(6) - Pb(1) - N(7)	155.4(4)	N(5)-Pb(1)-N(7)	78.2(3)
N(6)-Pb(1)-N(16)	82.2(4)	N(5)-Pb(1)-N(16)	69.7(3)
N(4)-Pb(1)-N(5)	64.6(3)	N(7)-Pb(1)-N(16)	94.5(4)
N(8) - N(6) - Pb(1)	115.1(10)	N(11)-N(7)-Pb(1)	115.5(8)
N(7)-N(11)-N(10)	177.2(14)	N(6)-N(8)-N(9)	179.2(18)

Table 3

Selected bond distances (Å) and bond angles (°) for **2**.

Bond distances			
Pb-N(1)	2.488(4)	N1A–C1A	1.168(7)
Pb-N(2)	2.460(4)	N1B-C1B	1.170(7)
Pb-N(3)	2.580(3)	S1A–C1A	1.623(6)
Pb-N1A	2.537(5)	S1B-C1B	1.634(6)
Pb-N1B	2.627(5)		
Bond angles			
N(2) - Pb - N(1)	65.67(13)	N(1B)-Pb-N(3)	81.02(14)
N(1)-Pb-N(3)	133.24(12)	N(1)-Pb-N(1A)	93.04(14)
N(2)-Pb-N(3)	68.61(12)	N(1A)-Pb-N(1B)	150.46(14)
N(2)-Pb-N(1B)	76.31(13)	N(1A)-C(1A)-S(1A)	178.9(5)
N(1)-Pb-N(1B)	79.33(14)	N(1B)-C(1B)-S(1B)	179.2(5)
N(1A)-Pb-N(3)	83.93(14)	C(1B)-N(1B)-Pb	124.0(4)
N(2)-Pb-N(1A)	74.57(13)	C(1A)–N(1A)–Pb	137.1(4)

bond lengths are larger than Pb–N(apical) distances (Tables 2 and 3). The quasi-linear pseudohalides are coordinated to lead(II) center in a bending fashion. In **1**, N(6)–N(8) and N(7)–N(11) bond lengths [1.18(2) and 1.199(16) Å] are larger than that [1.17(2) and 1.165(17) Å] in N(8)–N(9) and N(11)–N(10) confirming coordination of N(6) and N(7) to the lead(II) center. In **2**, N (N1A, N1B) atoms of the terminal thiocyanates are bound to the metal centers rather than S (S1A and S1B) atoms.

3.3. Thermal studies

To examine thermal stabilities of the compounds **1** and **2**, thermogravimetric (TG) and differential thermal analyses (DTA) were made between 30 and 750 °C in a static atmosphere of N₂. The thermal decomposition behaviours of both **1** and **2** are similar. **1** is stable up to 208 °C, whereas **2** shows thermal stability up to 240 °C. TG-DTA curve indicates gradual decomposition of the ligands in the 208–730 °C temperature range with an endothermic effect at 219 °C in **1** and in the 240–730 °C temperature range with an exothermic effect at 252 °C in **2**. In summary, the analyses show greater thermal stability of **2** over **1**.

3.4. Luminescence properties

The photoluminescence behaviours of the free Schiff base ligand (pbap) and its corresponding lead(II) pseudohalide compounds (**1** and **2**) were studied in DMF solutions at room temperature. The spectral patterns are depicted in Fig. 3. Upon photoexcitation at the corresponding absorption band (270 nm) in DMF solution, free ligand exhibits a broad fluorescent emission centered at 378 nm. However, **1** and **2** show a large red-shifted but more intense photoluminescence characteristics with main emissions respectively



Fig. 3. Emission spectra of: pbap, 1 and 2 (fluorescence in DMF solutions at 298 K).

at 426 and 418 nm upon excitation at the corresponding absorption bands (272 nm in **1** and 273 nm in **2**) of the compounds. The lifetimes are 2.56 (**1**) and 2.52 ns (**2**). The red shift (48 nm in **1** and 40 nm in **2**) as well as greater intensity of luminescence behaviour may be attributed [25] to the metal-perturbed intraligand ${}^{1}(\pi-\pi^{*})$ transition becoming more permissible upon coordination of the Schiff base.

4. Conclusions

We are able to prepare and X-ray crystallographically characterize two new luminous pentacoordinated neutral dinuclear compounds of lead(II) in concert with a Schiff base and pseudohalides through single-pot reactions of the molecular building units in preassigned ratios. The interesting feature is the bis(tridentate) coordination behaviour of the Schiff base bridging two metal ions. New variety of dinuclear compounds containing terminal pseudohalides is the result from such study.

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Appendix A. Supplementary data

Crystallographic data for the structural analyses (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center (CCDC Nos. 753619 for **1** and 753620 for **2**). Copies of this information can be had 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 http:// www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.molstruc.2009.12.015.

References

- (a) R.L. Davidovich, V. Stavila, D.V. Marinin, E.I. Voit, K.H. Whitmire, Coord. Chem. Rev. 253 (2009) 1316;
 - (b) D.-Q. Li, X. Liu, J. Zhou, Inorg. Chem. Commun. 11 (2008) 367;
 - (c) S. Hazra, S. Majumder, M. Fleck, R. Koner, S. Mohanta, Polyhedron 28 (2009)

2871;

- (d) J. Yang, J.-F. Ma, Y.-Y. Liu, J.-C. Ma, S.R. Batten, Cryst. Growth Des. 9 (2009) 1894.
- [2] (a) F. Marandi, B. Mirtamizdoust, A.A. Soudi, H.-K. Fun, Inorg. Chem. Commun. 10 (2007) 174;
 (b) C. Kazak, M.B. Arslan, S. Karabulut, A.D. Azaz, H. Namli, R. Kurtaran, J. Coord.
- (b) C. Razak, M.D. Alsian, S. Rafabulut, A.D. Azaz, H. Nahili, K. Rutafah, J. Colu Chem. 62 (2009) 2966.
- [3] (a) C. Platas-Iglesias, D. Esteban-Gomez, T. Enriquez-Perez, F. Avecilla, A.D. Blas, T. Rodriguez-Blas, Inorg. Chem. 44 (2005) 2224;
 (b) G.H. Shahverdizadeh, A.A. Soudi, A. Morsali, P. Retaillean, Inorg. Chim. Acta

361 (2008) 1875; (c) B. Ding, Y.Y. Liu, X.-J. Zhao, E.-C. Yang, X.G. Wang, J. Mol. Struct. 920 (2009) 248.

- [4] (a) Special issue on Molecular materials in electronic and optoelectronic devices, Acc. Chem. Res. 32 (1999) 3;
- (b) M. Petty, Molecular Electronics: From Principles to Practice, Wiley, Chichester, 2008.
- [5] J.J. Perry, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1400.
- [6] (a) T.K. Karmakar, S.K. Chandra, J. Ribas, G. Mostafa, T.-H. Lu, B.K. Ghosh, Chem. Commun. (2002) 2364;

(b) T.K. Karmakar, B.K. Ghosh, A. Usman, H.-K. Fun, E. Riviere, T. Mallah, G. Aromi, S.K. Chandra, Inorg. Chem. 44 (2005) 2391.

- [7] (a) S.H. Rahaman, R. Ghosh, T.-H. Lu, B.K. Ghosh, Polyhedron 24 (2005) 1525;
 (b) S.H. Rahaman, H.-K. Fun, B.K. Ghosh, Polyhedron 24 (2005) 3091;
 (c) S.H. Rahaman, H. Chowdhury, H.L. Milton, A.M.Z. Slawin, J.D. Woollins, B.K.
- Ghosh, Inorg. Chem. Commun. 8 (2005) 1031.
 [8] (a) T.K. Karmakar, G. Aromi, B.K. Ghosh, A. Usman, H.-K. Fun, T. Mallah, U.
- (a) L.K. Kalmakai, G. Alonin, D.K. Ghosh, A. Osman, H.-K. Fuli, T. Mahan, O. Behrens, X. Solans, S.K. Chandra, J. Mater. Chem. 16 (2006) 278; (b) S.H. Rahaman, D. Bose, R. Ghosh, G. Mostafa, H.-K. Fun, B.K. Ghosh, Struct. Chem. 18 (2007) 237:

(c) B.N. Sarkar, K. Bhar, S. Kundu, H.-K. Fun, B.K. Ghosh, J. Mol. Struct. 936 (2009) 104.

- [9] (a) A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1;
 - (b) V. Alexander, Chem. Rev. 95 (1995) 273;
- (c) P.A. Vigato, S. Tamburini, L. Bertolo, Coord. Chem. Rev. 251 (2007) 1311.
 [10] (a) A.M. Golub, H. Kohler, V.V. Skopenko (Eds.), Chemistry of Pseudohalides, Elsevier, Amsterdam, 1986;
 - (b) D.A. Buckingham, Coord. Chem. Rev. 135–136 (1994) 587;
- (c) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezana, T. Rojo, Coord. Chem. Rev. 193–195 (1999) 1027.
- [11] (a) S.S. Massoud, F.A. Mautner, M. Abu-Youssef, N.M. Shuaib, Polyhedron 18 (1999) 2287;

(b) S.S. Massoud, F.A. Mautner, Inorg. Chim. Acta 358 (2005) 3334;

(c) F.A. Mautner, F.R. Louka, T. LeGuet, S.S. Massoud, J. Mol. Struct. 919 (2009) 196.

[12] (a) U. Mukhopadhyay, I. Bernal, S.S. Massoud, F.A. Mautner, Inorg. Chim. Acta 357 (2004) 3673;

(b) F.A. Mautner, C.N. Landry, A.A. Gallo, S.S. Massoud, J. Mol. Struct. 837 (2007) 72;

(c) B. Samanta, J. Chakraborty, C.R. Choudhury, S.K. Dey, D.K. Dey, S.R. Batten, P. Jensen, G.P.A. Yap, S. Mitra, Struct. Chem. 18 (2007) 33;
(d) S.S. Massoud, K.T. Broussard, F.A. Mautner, R. Vecente, M.K. Saha, I. Bernal,

Inorg. Chim. Acta 361 (2008) 123.
[13] (a) S.S. Massoud, F.A. Mautner, R. Vicente, A.A. Gallo, E. Ducasse, Eur. J. Inorg. Chem. (2007) 1091;
(b) M.-L. Bonnet, C. Aronica, G. Chastanet, G. Pilet, D. Luneau, C. Mathoniere, R.

Clerse, V. Robert, Inorg. Chem. 47 (2008) 1127;

(c) Z.-L. Chen, C.-F. Jiang, W.-H. Yan, F.-P. Liang, S.R. Batten, Inorg. Chem. 48 (2009) 4674.

[14] (a) Y.-Q. Sun, D.-Z. Gao, W. Dong, D.-Z. Liao, C.-X. Zhang, Eur. J. Inorg. Chem. (2009) 2825;

(b) A.D. Khalaji, M. Weil, H. Hadadzadeh, M. Daryanavard, Inorg. Chim. Acta 362 (2009) 4837;

(c) M. Sarkar, R. Clerac, C. Mathoniere, N.G.R. Hearns, V. Bertolasi, D. Ray, Eur. J. Inorg. Chem. (2009) 4675.

- [15] H. Chowdhury, R. Ghosh, S.H. Rahaman, B.K. Ghosh, Polyhedron 26 (2007) 5023.
- [16] A. Mohamadou, G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Marrot, J. Reedijk, Polyhedron 28 (2009) 2813.
- [17] G.M. Sheldrick, SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
- [18] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
- [19] A.L. Spek, Acta Cryst. D 65 (2009) 148.
- [20] L.J. Farrugia, J. Appl Crystallogr. 30 (1997) 565.
- [21] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, fifth ed., John Wiley & Sons, New York, 1997.
- [23] (a) A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, New York, 1984;
 (b) J. Garcia Sole, L.E. Bausa, D. Jaque, An Introduction to the Optical
- Spectroscopy of Inorganic Solids, John Wiley & Sons, New York, 2005. [24] A.W. Addision, T.N. Rao, J. Reedijk, J.V. Rijn, G.C. Verschoor, J. Chem. Soc. Dalton
- Trans. (1984) 1349.
- [25] (a) B. Dutta, P. Bag, U. Florke, K. Nag, Inorg. Chem. 44 (2005) 147;
 - (b) S. Banthia, A. Samanta, J. Phys. Chem. B 110 (2006) 6437; (c) H.A. Habib, A. Hoffmann, H.A. Hoppe, G. Stelnfeld, C. Janiak, Inorg. Chem. 48 (2009) 2166.