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Unusual perchlorate binding in heptacoordinated cadmium(II)thiocyanate containing a pentadentate Schiff base

Sk Hafijur Rahaman [a], Rajarshi Ghosh [a], Golam Mostafa [b], Barindra Kumar Ghosh [a,*]

[a] *Department of Chemistry, The University of Burdwan, Golapbag, Rajbati, Burdwan 713 104, India*
[b] *Department of Physics, Jadavpur University, Kolkata 700 032, India*

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Abstract

A new Schiff base, *N*,*N*′-(bis(pyridin-2-yl)benzylidene)diethylenetriamine (bpbd), has been used to synthesise a novel heptacoordinated cadmium(II)thiocyanate complex [Cd(bpbd)(NCS)(ClO_4)] (**1**). Crystal structure analysis of **1** reveals cadmium(II) centre in a distorted pentagonal bipyramid environment with perchlorate binding, C–H···O hydrogen bonding and C–H···π interaction leading to a 2D sheet. **1** displays intraligand $^1(\pi-\pi^*)$ fluorescence and intraligand $^3(\pi-\pi^*)$ phosphorescence in glassy solutions (MeOH at 77 K).
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Keywords: Cadmium(II)thiocyanate; Schiff base; X-ray structure; Supramer; Luminescence

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The development of coordination polymers [1] with strong covalent bonds [2] and supramolecular entities [3] involving weak non-covalent forces [4] is an exciting area of research that has implications for the rational design of functional materials [5–7] at molecular level. Self-assembly [8] of the molecular components is the most efficient approach towards preparation of varied frameworks of complex connectivities via malleable coordination bonds and lateral multiple non-covalent forces. We are interested [9] in this approach for the construction of the inorganic functional polymers and supramers through variation of ligand backbone and metal ion coordination environment. Schiff bases have recently [9a,10] been focused by the coordination chemists as versatile organic blockers because of their preparative accessibilities, structural varieties and varied denticities. Pseudohalide like thiocyanate [11] is a putative ambidentate ligand and cadmium is well-suited [12–14] to this study as its d^{10} configuration permits a wide range of symmetries and coordination numbers. Report of six-coordinated Cd(II) complex [15] with perchlorate bindings by Jan Fábry et al. has prompted us to develop new luminous materials with superstructures via different non-covalent forces. This paper presents synthesis and X-ray structure of a new seven-coordinated luminous cadmium(II) complex [Cd(bpbd)(NCS)(ClO_4)] (**1**) through reaction of $Cd(ClO_4)_2 \cdot 6H_2O$, *N*,*N*′-(bis(pyridin-2-yl)benzylidene)diethylenetriamine (bpbd) and NH_4NCS in 1:1:1 molar ratio in MeOH–MeCN [16]. The interesting feature of this compound is enhanced coordination of the metal centre through perchlorate binding via one of its O atoms that ensures such a conformation to the whole coordination frame that C–H···O hydrogen bonding and C–H···π interaction occur leading to a superstructure.

The air-stable, moisture-insensitive complex is soluble in a range of common organic solvents but is insoluble in water. In IR, **1** displays splittings of $\nu_3(ClO_4)$ band at 1144, 1116, 1080 cm^{-1} and conductance measurement in MeCN solution it shows low Λ_M value

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[*] Corresponding author. Tel.: +91 342 2558545/6501; fax: +91 342 2530452.
E-mail address: barin_1@yahoo.co.uk (B.K. Ghosh).

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which is consonance with coordination of perchlorate ion in solid state as well as in solution. The X-ray diffraction study confirms this hypothesis. The solution of **1** in MeCN is colourless and exhibits absorption at 310 (sh) and 358 (sh) nm. Reflectance spectrum (310 and 359 nm) in nujol and electronic spectrum in MeCN solution are akin reflecting similar gross structure and electronic structure in solid state and in solution.

The structure determination reveals that **1** consists of 2D covalent chain through cooperative weak C–H···O hydrogen bonding and C–H···π interaction. An ORTEP diagram with atom numbering scheme of the mononuclear unit with stoichiometry [Cd(bpbd)(NCS)(ClO_4)] (**1**) is shown in Fig. 1, where each cadmium is uniquely heptacoordinated by a pentadentate Schiff base (bpbd), a terminal thiocyanate and a coordinating perchlorate anion. The coordination polyhedron around cadmium is best described as distorted pentagonal bipyramid with CdN_6O chromophore. Distortion from the ideal geometry is due to the asymmetric nature [17] of the bound Schiff base blocker and the deviations of the refine angles formed at the metal centre. The coordination includes the Schiff base ligated by two pyridine nitrogens (N2, N4), two imine nitrogens (N3, N5), one NH nitrogen (N6), a terminal thiocyanate nitrogen (N1) and an oxygen (O1) of the coordinated perchlorate anion. Five N atoms of bpbd and an N-donation of ambidentate NCS creates hardness in cadmium(II) centre to such an extent that it forces the perchlorate anion to bind the metal via covalent bond within the coordination sphere. This rare binding mode (Cd–O1) of the counter anion facilitates a heptacoordination around cadmium. The degrees of distortion from an ideal pentagonal bipyramidal geometry are reflected in the *equatorial* (67.13(16)–150.84(18)°) and the *axial* angles (171.4(2)°). The equatorial plane consists of N2, N3, N4, N5, N6 nitrogen atoms of pentadentate schiff base and the axial position occupied by N1 of thiocyanate and O1 of perchlorate. Cd–N distances are in the range (2.353(6)–2.457(5)) Å, comparable to the corresponding values in similar systems [11–14]. The Cd–O1 (2.692(5) Å) distance is much larger compared to the Cd–N distances. Angles subtended by the Schiff base blocker in the equatorial plane (67.14(17)–72.38(18)°) lie very close to the ideal angle (72.00°).The *trans* axial angle N1–Cd–O1 (171.4(2)°) deviates slightly from the 180.00°. There are two gauche five-membered rings: Cd, N5, C17, C16, N6 and Cd, N6, C15, C14, N3 and two coplanar five-membered rings: Cd, N2, C25, C18, N5 (rms deviation 0.069 Å) and Cd, N3, C7, C6, N4 (rms deviation 0.088 Å). The ethylenic parts of the Schiff base are to some extent puckered. All the bond angles and bond lengths on the ligand network are as expected [10]. The thiocyanate is coordinated in a linear fashion as seen from its N1–C1–S angle (177.4(7)°). The N1–C1 length (1.256(12) Å) is shorter than C1–S (1.455(9) Å) reflecting N-coordination of the pseudohalide. The closed C–H···π interaction [4] joins adjacent two molecules and three C–H···π interactions (Cg1: N2–C25–C26–C27–C28–C29; Cg2: N4–C2–C3–C4–C5–C6; Cg3: N8–C9–C10–C11–C12–C13) construct a supramoleculer chain (Fig. 2) running along *a*-axis (D–H···π: C9–H9···Cg1$^{(i)}$, C24–H24···Cg3$^{(ii)}$, C27–H27P···Cg2$^{(ii)}$; H···π: 3.00, 3.20, 3.23 Å; D···π: 3.730 (6), 3.910 (6), 3.695(6) Å; ∠D–H–π: 136°, 134°, 113°. The symmetry code: (i) $-1/2 + x$, y, $3/2 - z$; (ii) $1/2 + x$, y, $3/2 - z$). The chains (Fig. 2) are joined by a C–H···O interaction (C12–H12···O3^{i}) to form a 2D sheet in *ab*-plane (H···A: 2.49 Å, D···A: 3.417(10) Å, ∠D–H–A: 174°. The symmetry code: $2-x$, $1/2 + y$,

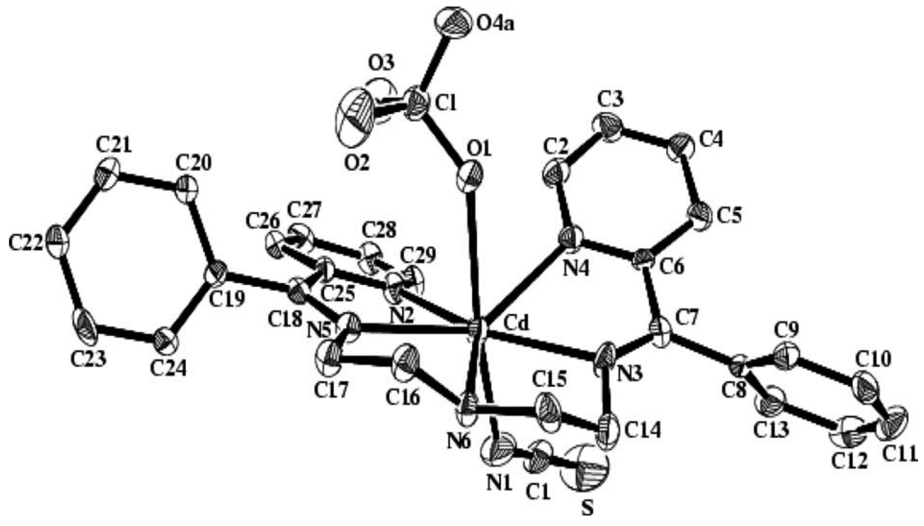

Fig. 1. The ORTEP diagram of **1** showing the atom labeling scheme (40% ellipsoids).

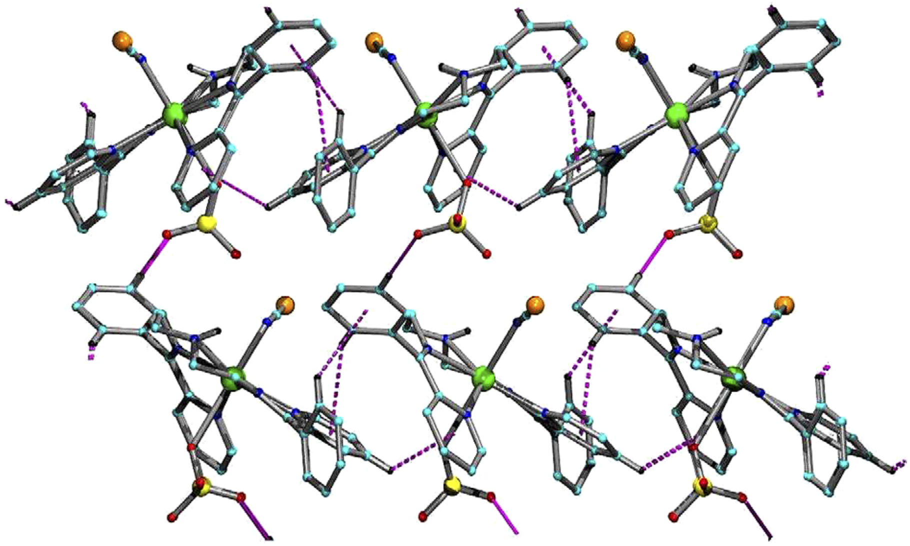

Fig. 2. 2D sheet formed by cooperative C–H···O hydrogen bonding and C–H···π interaction in *ab*-plane.

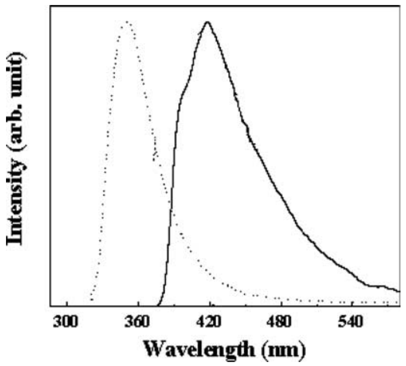

Fig. 3. Fluorescence (·······) of **1** in MeOH solution at 298 K, phosphorescence (——) in MeOH glassy solution.

$1-z$). This develops hydrogen, $H^{\delta+}$ character and the ortho hydrogen become activated and may be used in crystal engineering.

Complex **1** shows emission spectrum at 358 nm at 298 K (Fig. 3). These are assignable to intraligand $^1(\pi–\pi^*)$ fluorescence [13b]. The lifetimes of the complex is 2.63 ns. Complex **1** shows overall stronger weak interaction, this higher lifetime may be due to the presence of a stronger weak interactions which is mainly responsible for fluorescence. In glassy solutions (77 K), a red shift is observable (417 nm) for **1** which is presumably due to $^3(\pi–\pi^*)$ phosphorescence [9b].

In conclusion, we have synthesized a new luminous supramer through a single-pot reaction of the building components with preassigned ratio. Structure **1** represents the reliability of combination of strong and weak interactions in crystal engineering. In future, we will expand different molecular and crystalline architectures through tailoring on organic blocker and in combination with new terminals and/or bridges.

Acknowledgements

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References

[1] (a) P. Comba, T.W. Hambley, Molecular Modeling of Inorganic and Coordination Compounds, second ed., VCH, Weinheim, 2001;
(b) D.B. Mitzi, Prog. Inorg. Chem. 48 (1999) 1.

[2] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.

[3] (a) J.W. Steed, J.L. Atwood, Supramolecular Chemistry, Wiley, New York, 2000;
(b) T. Steiner, Angew. Chem., Int. Ed. 41 (2002) 48.

[4] (a) C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885;
(b) G.R. Desiraju, Accounts Chem. Res. 35 (2002) 565;
(c) H.W. Roesky, M. Andresh, Coordin. Chem. Rev. 236 (2003) 91.

[5] (a) B. Cornils, W.A. Herrmann, R. Schlogl (Eds.), Catalysis from A to Z: A Concise Encyclopedia, Wiley, New York, 2000;
(b) Special issue on Chemical Sensors, Chem. Rev. 100 (2000) No 7.

[6] (a) F.L. Caster, R.E. Siatowski, H. Woltzen (Eds.), Molecular Electronic Devices, North-Holland, Amsterdam, 1999;
(b) S.R. Marder, Metal Containing Materials for Non-linear Optics in Inorganic Materials, in: D.W. Bruce, D. O'Hare (Eds.), Wiley, Chichester, 1996.

[7] (a) C. Janiak, J. Chem. Soc., Dalton Trans. (2003) 2781;
(b) S.L. James, Chem. Soc. Rev. 32 (2003) 276.

[8] Special issue on Focus on self-assembly, Accounts Chem. Res. 4, 1999, 32.

[9] (a) T.K. Karmakar, S.K. Chandra, J. Ribas, G. Mostafa, T.-H. Lu, B.K. Ghosh, Chem. Commun. (2002) 2364;
(b) D. Bose, Sk.H. Rahaman, G. Mostafa, R.D. Bailey Walsh, M.J. Zaworotko, B.K. Ghosh, Polyhedron 23 (2004) 545.

[10] (a) V. Alexander, Chem. Rev. 95 (1995) 273;
(b) E.-Q. Gao, S.,-Q. Bai, Y.-F. Yue, Z.-M. Wang, C.-H. Yan, Inorg. Chem. 42 (2003) 3642.

[11] (a) A.M. Golub, H. Kohler, V.V. Skopenko (Eds.), Chemistry of Pseudohalides, Elsevier, Amsterdam, 1986;
(b) J.M. Clemente-Juan, B. Chansou, B. Donnadieu, J.-P. Tuchagues, Inorg. Chem. 39 (2000) 5515.

[12] (a) G. Mostafa, A. Mondal, A. Ghosh, I.R. Laskar, A.J. Welch, N. Ray Chaudhuri, Acta Cryst. C 56 (2000) 146;
(b) B.G. Chand, U.S. Ray, G. Mostafa, T.-H. Lu, C.R. Sinha, Polyhedron 23 (2004) 1669.

[13] (a) R. Wang, M. Hong, D. Yuan, Y. Sun, L. Xu, J. Luo, R. Cao, A.S.C. Chan, Eur. J. Inorg. Chem. (2004) 37;
(b) X. Shi, G. Zhu, Q. Fang, G. Wu, G. Tian, R. Wang, D. Zhang, M. Xue, S. Qiu, Eur. J. Inorg. Chem. (2004) 185.

[14] (a) J. Granifo, M.T. Garland, R. Baggio, Inorg. Chem. Commun. 7 (2004) 77;
(b) D. Bose, J. Banerjee, Sk.H. Rahaman, G. Mostafa, H.-K. Fun, R.D. Bailey Walsh, M.J. Zaworotko, B.K. Ghosh, Polyhedron 23 (2004) 2045.

[15] V. Haber, I. Císaová, J. Fábry, Polyhedron 22 (2003) 3451.

[16] Synthesis of [Cd(bpbd)(NCS)(ClO_4)] (**1**): An acetonitrile solution (10 ml) of faint yellow bpbd (0.433 g, 1 mmol) was added dropwise to a colourless methanolic solution (5 ml) of cadmium(II) perchlorate hexahydrate (0.311 g, 1 mmol). To this light yellow solution, ammonium thiocyanate (0.076 g, 1 mmol) in methanol (5 ml) was added slowly. The faint yellow solution was filtered and left for slow evaporation in air. After two days fine transparent light yellow single crystals of compound **1** separated out, which were filtered, washed with methanol and dried in vacuo over $CaCl_2$. The yield was 0.527 g (75%). Found: C, 49.35; H, 3.63; N, 12.18%; Anal. Calc. for $C_{29}H_{27}N_6O_4SClCd$ (**1**): C, 49.51; H, 3.87; N, 11.95%. Λ_M(MeCN): 60 Ω^{-1} cm^2 mol^{-1}. IR (KBr disc, 4000–300 cm^{-1}): ν(NH) 3294, ν(CN) 2070, ν(C=N) 1629, 1590, ν(ClO_4) 1144, 1116, 1080, 622. UV–Vis (MeCN): λ_{max}, 310 (sh) and 358 (sh) nm. The crystal data for **1**: Formula: $C_{29}H_{27}N_6O_4SClCd$, size: $0.35 \times 0.18 \times 0.11$ mm^3, *Fw*: 703.48, orthorhombic, $Pn2_1a$, $a = 16.8378(17)$, $b = 16.6192(17)$, $c = 10.6352(12)$ Å, $T = 294(2)$ K, $V = 2976.1(5)$ Å^3, $Z = 4$, $D_c = 1.570$ mg m^{-3}, final R indices [$I > 2\sigma$ (I)]: $R^1 = 0.0760$, $wR^2 = 0.0675$, R indices (all data): $R^1 = 0.1001$, $wR^2 = 0.0425$, GOF = 1.000, Residual electron density (largest diff. Peak and hole) = 0.593 and −0.347 e A^{-3}, weighting scheme: $R^1 = \sum|F_o| - |F_c||/\sum|F_o$, $wR^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, Calc. $w = 1/[\sigma^2(F_o^2) + (0.0170P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$, $F(0\ 0\ 0) = 1424$, $T_{max}/T_{min} = 0.816/0.902$, Data/restraints/parameters = 6592/1/388, Siemens SMART CCD diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Reflections collected: 6592, unique reflections: 3603 were recorded using the ω-scan technique. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-211534 (**1**). Copies of this information can 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).

[17] S. Banerjee, A. Ghosh, B. Wu, P.-G. Lassahn, C. Janiak, Polyhedron. 24 (2005) 593.