

A Hyperbranched Polymer of Cadmium†**Arunendu Mondal,^a Golam Mostafa,^b Ashutosh Ghosh^c and Nirmalendu Ray Chaudhuri^{*a}**^aDepartment of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India^bX-ray Crystallography Laboratory, Department of Solid State Physics, Indian Association for the Cultivation of Science, Calcutta 700 032, India^cDepartment of Chemistry, University College of Science and Technology, Calcutta 700 009, India

Crystal structure analysis of Cd(aepn)(NCS)₂ [aepn = (2-aminoethyl)(3-aminopropyl)amine] reveals that each cadmium(II) possesses distorted octahedral geometry and is linked to four different nearest cadmium centres *via* thiocyanate groups and non-chelated arms of the triamine ligands forming a chain linked system of a hyperbranched polymeric molecule.

Cannas *et al.*^{1,2} reported the synthesis and single crystal structure of triamine complexes of cadmium(II) thiocyanate. They proposed the structure of Cd(aepn)(NCS)₂ [aepn = (2-aminoethyl)(3-aminopropyl)amine; NH₂CH₂CH₂NHCH₂CH₂CH₂NH₂] as a discrete five coordinated species on the basis of a *0kl* Weissenberg photograph.² Recently we synthesized these complexes to explore their thermal behaviour in the solid state.³ Interestingly we found that Cd(aepn)(NCS)₂ upon heating undergoes melting and remains a supercooled liquid at room temperature. Such a novel behaviour led us to explore the exact molecular structure. The structure is a three dimensional polymer, the synthesis and characterisation of which is of great current interest in the search for molecular based materials.^{4–7} The novelty of this compound is that it is a branched molecule synthesized in a single step, often called a hyperbranched polymer.^{8–10}

The structure determination reveals that the complex has stoichiometry, Cd(aepn)(NCS)₂ with the occurrence of Cd–N1–C1–S1–Cdⁱ (*i* = –*x* + 1, *y* – 1/2, –*z* + 1/2) zigzag infinite chains along crystallographic direction *b* and Cd–N4–C5–C6–C7–N5–Cdⁱⁱ (*ii* = –*x* + 1/2, –*y* + 1, *z* – 1/2) along *c*. An ORTEP view with the atom numbering scheme showing the hyperbranched polymeric structure of the molecule is shown in Fig. 1, where each cadmium acts as a centre of branching. One of the thiocyanate groups (N1C1S1) bridges in the μ (N,S) mode to the nearest cadmium centres and the other (N2C2S2) is monodentate through N2. The ethylenic part of the ligand is chelated to form a five membered ring and the propylenic arm is used as a non-chelating end to bridge another adjacent cation. Thus each cadmium centre is linked to four different nearest cadmium centres *via* thiocyanate groups and non-chelated arms of the triamine ligands to form a chain linked system of a polymeric molecule. Each cadmium atom possesses distorted octahedral geometry. Two nitrogen atoms (N3, N4) of the chelated portion of the aepn, one symmetry related nitrogen atom (N5ⁱⁱⁱ, *iii* = –*x* + 1/2, –*y* + 1, *z* + 1/2) of the non-chelated portion of the amine and one nitrogen atom (N2) of the terminal thiocyanate group (N2C2S2) define the equatorial plane. The apical positions of the octahedron are occupied by one nitrogen (N1) of the bridging thiocyanate group (N1C1S1) and the symmetry related sulfur atom (S1^{iv}, *iv* = –*x* + 1, *y* + 1/2, –*z* + 1/2). The degrees of distortion from an ideal octahedral geometry

are reflected in the cisoid [85.1(2)–104.9(3)°] and the transoid angles [164.1(3)–175.9(3)°].

The five membered chelate ring Cd–N3–C3–C4–N4 adopts an open envelope geometry with C3 on the flap, 0.594 Å away from the least squares plane defined by the other four ring atoms. The Cd–N distances are in the range 2.306(8)–2.393(7) Å comparable to corresponding values in similar systems.^{1,2} The Cd–S1 distance (2.723 Å), Cd–N1–C1 (168.6°) and Cd–N2–C2 angles (160.8°) are significantly different from those reported [Cd–S 2.93 and 2.80 Å, Cd–N–C(NCS) 140°] by Cannas *et al.*¹ The thiocyanate ligands are almost linear. Other bond lengths and angles in the ligand are close to expected values.

The conclusion made by Cannas *et al.*² for the structure of Cd(aepn)(NCS)₂ on the basis of a *0kl* Weissenberg photograph was not correct. Determination of the crystal structure clearly show that it is a polymeric molecule where each cadmium centre possesses distorted octahedral geometry.

In Cd(dien)(NCS)₂¹ [dien = bis(2-aminoethyl)amine] the NCS groups are linked to adjacent cadmiums as the amine arm of dien has the right length to bridge the Cd–NCS–Cd chain and make it a one dimensional polymer. Here simultaneous bridging through the propylenic arms of aepn and thiocyanate group between the two adjacent cations does not occur as the length of the former is not compatible with the bridged Cd–NCS–Cd chain. As a result

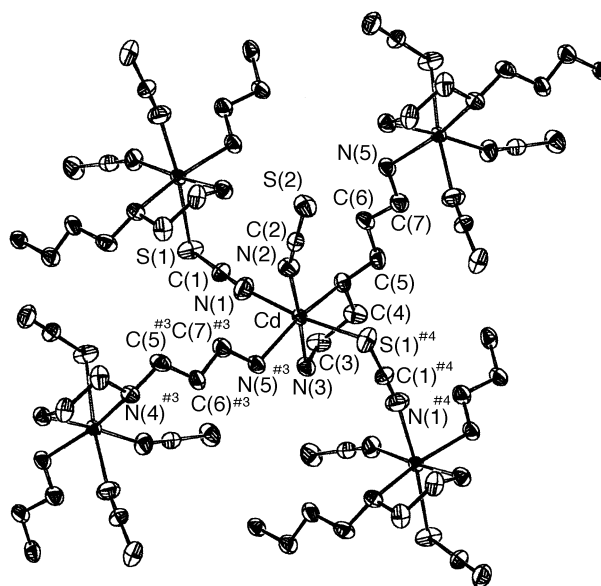


Fig. 1 ZORTEP plot of Cd(aepn)(NCS)₂ with atom numbering scheme; 3 –*x* + 1/2, –*y* + 1, *z* + 1/2; 4 –*x* + 1, *y* + 1/2, –*z* + 1/2

*To receive any correspondence (e-mail: icnrc@iacs.ernet.in).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for other atoms) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Cd(aepn)(NCS)₂; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Cd	40 232(6)	56 261(4)	24 249(3)	20(1)
S1	7771(3)	2299(2)	3433(2)	39(1)
C1	6429(11)	3316(7)	3197(6)	28(2)
N1	5503(13)	4057(7)	3020(7)	45(2)
S2	-625(3)	3542(2)	657(2)	43(1)
C2	824(12)	4081(7)	1359(6)	30(2)
N2	1864(11)	4467(7)	1858(6)	38(2)
N3	6336(10)	6717(6)	3079(5)	32(2)
C3	7920(10)	6421(8)	2563(7)	35(2)
C4	7527(12)	6485(8)	1525(7)	37(2)
N4	6207(9)	5638(6)	12695	27(1)
C5	5702(13)	5761(8)	319(6)	35(2)
C6	4611(13)	4794(8)	-32(6)	34(2)
C7	3606(12)	5043(8)	-886(6)	33(2)
N5	2531(10)	4121(6)	-1210(5)	30(2)

a three dimensional branched polymeric molecule is formed by Cd(aepn)(NCS)₂. This is the first ever example where aepn forms only one chelate ring and uses the non-chelating end to bond to another metal atom.

Experimental

(2-Aminoethyl)(3-aminopropyl)amine(aepn) was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were of AR grade.

Synthesis of Cd(aepn)(NCS)₂.—This was synthesized³ by adding the ligand (2 mmol) dissolved in ethanol (5 ml) to an ethanolic (5 ml) solution of cadmium(II) thiocyanate (2 mmol) and filtered. The filtrate was kept in a CaCl₂ desiccator. After a few days the colorless shining crystals which separated were filtered off, washed with ethanol and dried in a CaCl₂ desiccator. Yield 75% (Found: C, 24.5; H, 4.2; Cd, 32.3; N, 20.2; S, 18.4; Calc. for C₇H₁₅CdN₅S₂: C, 24.3; H, 4.3; Cd, 32.5; N, 20.3; S, 18.5%)

Crystal Structure Analysis.—Single crystals were obtained by recrystallisation of [Cd(aepn)(NCS)₂]_n from ethanol. A crystal suitable for X-ray analysis was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and Cu-K α (λ 1.5418 Å) radiation. The unit cell parameters and crystal orientation matrix were determined by least squares refinements of the setting angles of 25 reflections ($10 < \theta < 40^\circ$). Crystal and instrument stabilities were monitored with a set of three standard reflections measured over 100; in all cases variations were insignificant. The collected intensity data were corrected for Lorentz-polarisation effects¹¹ and an empirical absorption correction was also employed (T_{min}/T_{max} 0.6062/0.9841). Atomic coordinates are in Table 1.

The structure was solved by the Patterson method followed by successive Fourier synthesis and refined through full-matrix least squares on F^2 using SHELXL 93¹² with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms (C-H 0.97, N-H 0.900 Å) with an isotropic displacement parameter equal to 1.5 times the equivalent isotropic displacement parameter of their parent atoms. The refinement of 137 least-squares variables converged to residual indices $R1 = 0.0467$, $wR = 0.1158$ with $I > 2\sigma(I)$. The final Fourier difference map

showed maximum and minimum peak heights at 2.156 and $-1.430 \text{ e \AA}^{-3}$, respectively. The largest one, being within 1.03 Å of the cadmium atoms, had no chemical significance. The largest shift/esd in the final cycle of refinement was 0.062. Complex neutral-atom scattering factors were used.¹³ All calculations were carried out using the SHELX 86,¹⁴ SHELXL 93,¹² PARST¹⁵ and ZORTEP¹⁶ programs.

Crystal data.—C₇H₁₅CdN₅S₂, orthorhombic space group $P2_12_12_1$, $a = 7.652(3)$, $b = 11.926(6)$, $c = 14.498(3)$ Å, $V = 1323.1(9)$ Å³, $Z = 4$; $D_c = 1.736 \text{ g cm}^{-3}$, $\mu = 16.007 \text{ mm}^{-1}$, $F(000) = 688$; reflections collected 1575, independent reflections 1575, θ range for data collection 4.80–74.50°, data/restraints/parameters 1519/0/137; goodness of fit on F^2 1.039; $R1 = 0.0696$, $wR2 = 0.3456$; (all data); absolute structure parameter¹⁷ 0.02(2); extinction coefficient 0.0017(3). Full crystallographic details excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors. *J. Chem. Research (S)*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/10.

The authors are grateful to All India Institute of Medical Sciences and Department of Science and Technology for providing single crystal data. Funding for the work described was provided by the Council of Scientific and Industrial Research (New Delhi) Grants Scheme.

Received, 17th April 1998; Accepted, 26th May 1998
Paper E/8/02885K

References

- M. Cannas, G. Carta, A. Cristini and G. Maronigiu, *Inorg. Chem.*, 1977, **16**, 228.
- M. Cannas, A. Cristini and G. Maronigiu, *Inorg. Chim. Acta*, 1977, **22**, 233.
- A. Mondal, C. Pariya, A. Ghosh and N. Ray Chaudhuri, *Thermochim. Acta*, 1996, **287**, 165.
- B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and E. E. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1994, 1049.
- T. Soma, H. Yuge and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1665.
- M. Fujita, Y. J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1994, 1977.
- R. D. Bailey and W. T. Pennington, *Polyhedron*, 1997, **16**, 417.
- P. J. Flory, *J. Am. Chem. Soc.*, 1952, **74**, 2718.
- T. M. Miller, T. X. Neenan, E. W. Kwock and S. M. Stein, *J. Am. Chem. Soc.*, 1993, **115**, 356.
- M. Maciejewski, *J. Macromol. Sci., Chem.*, 1982, **A17**, 689.
- A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- G. M. Sheldrick, SHELXL 93, Program for the Solution of Crystal Structure, University of Göttingen, 1993.
- International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C, Tables 4.2.6.8 and 6.1.1.4.
- G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.
- M. Nardelli, *Comput. Chem.*, 1983, **7**, 1995.
- L. Zsolnai, ZORTEP, A program for the presentation of thermal ellipsoids, University of Heidelberg, 1994.
- H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.