

# Crystal Structure of *catena*-Poly-(thiocyanato-*N*)cadmium-di- $\mu$ -(thiocyanato-*N*)-(thiocyanato-*N*)cadmium-tris- $\mu$ -(4-*t*-butyl-1,2,4-triazole-*N*<sup>1</sup>:*N*<sup>2</sup>).<sup>†</sup> A New, Alternating *zig-zag* Chain containing N-Bonded, Bridging Thiocyanate

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The structure of  $[\text{Cd}_2(\text{NCS})_4(\text{butrz})_3]_\infty$  ( $\text{butrz} = 4\text{-}t\text{-butyl-1,2,4-triazole}$ ) consists of a *zig-zag* chain with alternating bridges of three *butrz* groups and two unusual N-bonded isothiocyanate anions; the octahedral co-ordination around each cadmium ion is completed by a monodentate isothiocyanate anion.<sup>‡</sup>

Thiocyanates are ambidentate ligands,<sup>1</sup> that can co-ordinate to metal ions *via* the N-atom or the S-atom.<sup>2</sup> In cases of low metal-to-ligand ratios, the NCS<sup>-</sup> ion bridges between metal ions, such as in compounds  $\text{M}(\text{NCS})_2\text{L}_2$  in which units  $\text{M}(\text{NCS})_2\text{M}$  occur in linear chains.<sup>3</sup> Bridging *via* the N-atom has only been reported for the ion  $[\text{Re}_2(\text{NCS})_{10}]^{3-}$  in which short M-M bonds occur.<sup>4</sup> A  $\nu(\text{CN})$  absorption below 2000  $\text{cm}^{-1}$  appears to be indicative for this bonding mode. 1,2,4-Triazoles are versatile ligands that usually form bridges between metal ions, resulting in dimers,<sup>5</sup> trimers,<sup>6</sup> or two-dimensional layered structures. In the latter case the triazole bridges through its N-1 and N-4 atoms.<sup>7</sup> In the bi- and trinuclear compounds, 1,2-bi-co-ordination occurs.

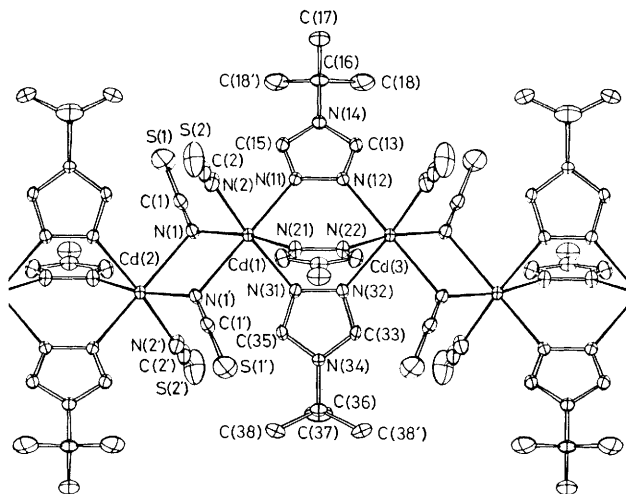
We now describe the synthesis, structure, and spectroscopic properties of a very unusual chain compound, containing alternating bridging units of triazole (N-1, N-2) ligands and N-bonded thiocyanate ions.  $[\text{Cd}_2(\text{NCS})_4(\text{butrz})_3]_\infty$  ( $\text{butrz} = 4\text{-}t\text{-butyl-1,2,4-triazole}$ ) was prepared by rapid addition of a

solution of  $\text{NH}_4\text{SCN}$  (5 mmol) and *butrz* (5 mmol) in 20 ml of water, to a boiling solution of  $\text{Cd}(\text{NO}_3)_2$  (2.5 mmol) in water (15 ml). After reduction of the volume to 30 ml, yellow crystals of the title compound were formed after several days at ambient temperature. The product was characterized by elemental analyses (Cd, C, H, N) and i.r. spectroscopy.<sup>‡</sup>

To understand the unusual i.r. spectra in the  $\nu_{\text{CN}}$  region, where a doublet at 2038 and 1982  $\text{cm}^{-1}$  is found, a crystal structure determination was undertaken. The structure was refined<sup>§</sup> from single-crystal diffractometer data using the program DIRDIF.<sup>8</sup> Part of the structure is shown in Figure 1. Each cadmium ion is six-co-ordinated by three triazole ligands (bidentate bridging), one monodentate N-bonded thiocyanate, and two atoms of bridging thiocyanate ligands. Cd-N distances are given in the caption of Figure 1, and are normal for Cd-NCS and Cd-N(azole) distances.<sup>9,10</sup> The carbon atoms of one of the *t*-butyl groups show some disorder, although no alternative positions were tried.

The bridging unit  $\text{Cd}(\text{NCS})_2\text{Cd}$  is highly unusual and in fact has not been observed before, except in the metal-bonded mixed-valence system  $[\text{Re}_2(\text{NCS})_{10}]^{3-}$ , where the Re-Re distance is about 2.61 Å with a Re-N-Re angle of 77.4°. This compound also has an unusual i.r. spectrum below 2000  $\text{cm}^{-1}$  (bands at 1920  $\text{cm}^{-1}$  and 1885  $\text{cm}^{-1}$ ).<sup>4</sup> A few other compounds also have NCS ligands with indications of N-bridging,<sup>11</sup> but in these cases one or both of the M-N bonds are extremely long and no i.r. bands below 2000  $\text{cm}^{-1}$  have been found. Therefore the title compound is the first with N-bonded, bridging thiocyanate ligands without metal-metal bonding.

The origin for this type of bonding in the present compound is not fully understood, because similar compounds with other



**Figure 1.** ORTEP drawing of a part of the  $[\text{Cd}_2(\text{NCS})_4(\text{butrz})_3]_\infty$  chain. The hydrogen atoms and a part of the *t*-butyl group of butrz ring 2 have been omitted for clarity; Cd(1)-Cd(2) 3.6912(4), Cd(1)-Cd(3) 4.0949(4) Å, Cd(1)-N(1)-Cd(2) 100.83(9)°. Bond distances to Cd(1) are: N(1) 2.352(3), N(1') 2.437(3), N(2) 2.240(3), N(11) 2.366(2), N(21) 2.368(3), and N(31) 2.350(2) Å. Bond angles around Cd(1) vary from 79 to 97° and from 169 to 170°. Cd(3) is related to Cd(1) by symmetry operation  $-x, \frac{1}{2}-y, z$ ; Cd(2) is related to Cd(1) by symmetry operation  $-x, -y, -z$ .

<sup>†</sup> The title compound has been named according to recent IUPAC advice for polymeric co-ordination compounds (*Pure Appl. Chem.*, 1981, **53**, 2283). Using the Inorganic Chemistry Nomenclature Rules of 1970, the name of the title compound would be: *catena*-tris- $\mu$ -(4-*t*-butyl-1,2,4-triazole-*N*<sup>1</sup>,*N*<sup>2</sup>)-di- $\mu$ -(thiocyanato-*N*)-di(thiocyanato-*N*)dicadmium(II).

<sup>‡</sup> I.r. bands (KBr disc) are observed at (strong bands only): 3118, 2975, 2038, 1982, 1535, 1525, 1467, 1460, 1375, 1346, 1210, 1063, 1020, 996, 895, 880, 855, 660, and 653  $\text{cm}^{-1}$ . The bands at 2038 and 1982  $\text{cm}^{-1}$  are due to the N-bonding and N-bridging NCS groups respectively. Additionally weaker bands, assigned to the NCS groups, are found at: 1940(sh), 802, 525, 498, 480, and 465  $\text{cm}^{-1}$ .

<sup>§</sup> *Crystal data*:  $(\text{C}_{22}\text{H}_{33}\text{Cd}_2\text{N}_{13}\text{S}_4)_\infty$ ; orthorhombic, space group *Pnma*,  $a = 10.898(1)$ ,  $b = 14.413(2)$ , and  $c = 21.402(2)$  Å,  $Z = 4$  (calculated on the basis of 2 Cd per formula unit and  $D_m = 1.65 \text{ g cm}^{-3}$ ) for  $D_c = 1.646 \text{ g cm}^{-3}$ . Intensities of 2682 independent reflections [with  $I > 2\sigma(I)$ ] were obtained (Mo- $K_\alpha$  radiation) on a crystal of dimensions  $0.4 \times 0.2 \times 0.2$  mm. The structure was solved using standard techniques and refined using full matrix least-squares to a final  $R$  value of 0.0227. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication no. [SUP 23348 (7 pp.)] from the British Library Lending Division. For details see Notice to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, index issues.

metal ions have not yet been prepared. In the case of the thiocyanates of Mn<sup>II</sup> to Zn<sup>II</sup>, either monomers,<sup>12</sup> dimers, or trimers were obtained in which the bridging is performed only by triazole ligands.<sup>13</sup> Crystal packing effects may be responsible for the particular structure in the case of Cd<sup>II</sup>, suggesting that other (magnetically interesting) metal ions might yield similar compounds with other, substituted triazole ligands.

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