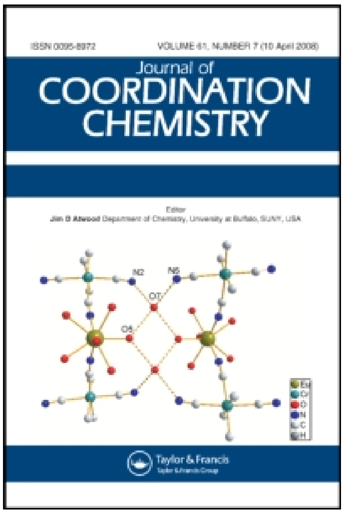

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Synthesis and Crystal Structure of a Polymeric Heteronuclear Complex of Cadmium(II) and Silver(I)

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SYNTHESIS AND CRYSTAL STRUCTURE OF A POLYMERIC HETERONUCLEAR COMPLEX OF CADMIUM(II) AND SILVER(I)

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A polymeric complex of Cd(II) and Ag(I) bridged by thiocyanate and ethylenediamine, $[Cd(en)_{1.5}Ag(SCN)_3]$, has been prepared and its structure determined by X-ray diffraction methods. The complex crystallizes in space group $P2_1/n$ with $a = 7.456(1)$, $b = 9.915(2)$, $c = 19.822(2)$Å, $\beta = 98.94(1)°$. The Cd(II) atom is octahedrally coordinated by three SCN^- anions and two en molecules, while the Ag(I) atom is tetrahedraly coordinated by four SCN^- anions. Both SCN^- anions and en molecules act as bridging ligands and link Ag(I) and Cd(II) atoms to form a three-dimensional polymeric structure. The distance between Ag(I) and the atom S of a 1,1,3-μ_3-SCN^- anion is much longer than that between Ag(I) and the atom S of a 1,3-μ-SCN^- anion. The short Ag—Ag distance of 3.133 Å and small Ag—S—Ag angle of 70.92° strongly suggests the existence of an Ag—Ag bonding interaction in the complex.

Keywords: Cadmium(II); Silver(I); Crystal structure; Thiocyanate; Polymeric complex

INTRODUCTION

With ambidexterous character, the SCN^- anion is expected to show a rich variety of coordination modes. The ability of SCN^- to form metal complexes in a monodentate mode [M-NCS or M-SCN] and in a μ-1,3-SCN^- bidentate bridging mode [M-NCS-M] has been extensively investigated [1–3]. A few complex structures with 1,1,3-μ_3-SCN^- or 1,1,1,3-μ_4-SCN^- bridging ligands have been reported, and in which an S atom bonds

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two or three metal atoms while an N atom bonds one metal atom [4–6]. During an investigation of heteronuclear complexes, we prepared a new complex with the 1,1,3-μ_3 bridging mode. Herein we present the synthesis and crystal structure of a heteronuclear complex of Ag(I) and Cd(II).

EXPERIMENTAL

Preparation

Fresh solid AgSCN (about 1.0 mmol), prepared by a reaction of $AgNO_3$ with equimolar KSCN in aqueous solution, was dissolved in 10.0 cm^3 aqueous solution containing KSCN (about 2.0 mmol) with continuous stirring. The resulting solution was added to an aqueous solution (10.0 cm^3) containing $CdCl_2 \cdot 2.5H_2O$ (1.0 mmol) and ethylenediamine (en) (2.0 mmol) with stirring at room temperature. The solid product was separated by filtration and dried under vacuum. C, H and N analyses with an Erba 1160 instrument supported the formulation of the product as $Cd(en)_{1.5}Ag(SCN)_{3.}$ *Anal.* Calcd. for $C_6H_{12}N_6S_3AgCd$(%): C, 14.88; H, 2.48; N, 17.36. Found: C, 15.05; H, 2.73; N, 17.01. Infrared spectra were recorded using a Nicolet 205 spectrophotometer (4000–400 cm^{-1}) with a powered sample spread on KBr plates.

Crystal Structure Determination

A single crystal with dimensions 0.44 × 0.40 × 0.36 mm was mounted on a glass fibre. Diffraction intensity data were collected on a Siemens P4 diffractometer up to $(2\theta)_{\max}$ of 52.0° with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan technique. A total of 3372 independent reflections was collected, of which 2346 were considered as observed [$I > 2\sigma(I)$] and used for the structure refinement. Usual Lp and empirical adsorption corrections were applied.

The structure was solved by direct methods followed by Fourier syntheses. The structure was refined on F^2 by full-matrix least-squares methods. H atoms were located in a difference Fourier map. Anisotropic refinement including all non-H atoms, using the SHELXTL software package [7], converged to agreement factors $R = 0.032$ and $R_w = 0.078$, where $w = 1/[\sigma^2(Fo^2) + (0.040\,P)^2 + 2.12\,P]$. The highest peak in the final difference Fourier map was 0.96 eÅ^{-3}. Atomic scattering factors used were taken from International Tables for X-ray crystallography [8].

RESULTS AND DISCUSSION

Crystal Structure

Crystal Data

$C_6H_{12}N_6S_3AgCd$, $M = 484.67$, monoclinic, space group $P2_1/n$, $a = 7.456(1)$, $b = 9.915(2)$, $c = 19.822(2)$ Å, $\beta = 98.94(1)°$, $V = 1447.6(4)$ Å^3, $Z = 4$, $D_c = 2.224\ \mathrm{g\,cm^{-3}}$, $F(000) = 932$, $\mu(\mathrm{MoK}\alpha) = 3.241\ \mathrm{mm^{-1}}$.

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are listed in Table II.

A perspective view of the molecular structure is illustrated in Figure 1, together with the atom numbering scheme. Four SCN^- anions coordinate to the Ag(I) atom with distorted tetrahedral geometry, S–Ag–S angles varying from 93.20 to 128.10°. Three SCN^- anions and two en molecules complete octahedral coordination around the Cd(II) atom.

Both SCN^- anions and en molecules act as bridging ligands in the complex. As expected from Pearson's principle of hard and soft Lewis acids and bases [9], the softer S atom of the SCN^- anion bonds to the softer Ag(I) atom while the harder N atom bonds to the Cd(II) atom. The en molecule bridges adjacent Cd(II) atoms and the SCN^- anion links Cd(II) and Ag(I) atoms to form a three-dimensional structure (Fig. 2). Two kinds of SCN^-

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Cd	1964(1)	1112(1)	1704(1)	37(1)
Ag	5987(1)	3890(1)	– 369(1)	58(1)
S(1)	6629(2)	4281(2)	952(1)	52(1)
S(2)	9015(2)	4332(2)	– 731(1)	57(1)
S(3)	3906(2)	1872(2)	– 658(1)	86(1)
N(1)	4081(6)	2719(5)	1498(2)	57(1)
N(2)	8429(6)	4014(5)	– 2143(2)	63(1)
N(3)	6218(6)	596(5)	– 1424(2)	60(1)
N(4)	– 306(5)	– 338(4)	1981(2)	51(1)
N(5)	– 35(5)	2575(4)	2132(2)	45(1)
N(6)	804(6)	1519(5)	524(2)	54(1)
C(1)	5096(6)	3343(5)	1256(2)	41(1)
C(2)	8634(6)	4117(5)	– 1567(2)	43(1)
C(3)	5291(7)	1099(5)	– 1097(2)	48(1)
C(4)	– 1826(7)	528(7)	2120(3)	68(2)
C(5)	– 1198(7)	1751(6)	2506(3)	65(2)
C(6)	– 393(8)	682(5)	39(3)	60(1)

TABLE II Bond lengths (Å) and angles (°) for the complex

Cd–N(1)	2.324(4)	Cd–N(2C)	2.379(4)
Cd–N(3B)	2.290(4)	Cd–N(4)	2.350(4)
Cd–N(5)	2.333(4)	Cd–N(6)	2.399(4)
Ag–S(1)	2.616(1)	Ag–S(1A)	2.780(2)
Ag–S(2)	2.512(1)	Ag–S(3)	2.542(2)
Ag–Ag(A)	3.133(1)	S(1)–C(1)	1.658(5)
S(2)–C(2)	1.650(4)	S(3)–C(3)	1.640(5)
N(1)–C(1)	1.139(6)	N(2)–C(2)	1.133(6)
N(3)–C(3)	1.134(6)	N(4)–C(4)	1.481(7)
N(5)–C(5)	1.472(6)	N(6)–C(6)	1.463(6)
C(4)–C(5)	1.471(8)	C(6)–C(6D)	1.492(11)
N(1)–Cd–N(2C)	89.0(2)	N(I)–Cd–N(3B)	91.2(2)
N(1)–Cd–N(4)	173.9(2)	N(1)–Cd–N(5)	97.3(2)
N(1)–Cd–N(6)	82.2(1)	N(2C)–Cd–N(3B)	89.6(2)
N(2C)–Cd–N(4)	89.1(2)	N(2C)–Cd–N(5)	84.6(2)
N(2C)–Cd–N(6)	171.2(2)	N(3B)–Cd–N(4)	94.6(2)
N(3B)–Cd–N(5)	169.6(2)	N(3B)–Cd–N(6)	91.5(2)
N(4)–Cd–N(5)	76.8(2)	N(4)–Cd–N(6)	99.6(1)
N(5)–Cd–N(6)	95.5(2)	S(1)–Ag–S(2)	103.16(4)
S(1)–Ag–S(3)	110.63(5)	S(1)–Ag–S(1A)	109.08(3)
S(1A)–Ag–S(2)	111.76(5)	S(1A)–Ag–S(3)	93.20(6)
S(2)–Ag–S(3)	128.10(5)	Ag–S(I)–C(1)	104.6(2)
AgA–S(1)–C(1)	92.2(2)	Ag–S(2)–C(2)	104.0(2)
Ag–S(3)–C(3)	94.3(2)	Ag–S(1)–AgA	70.92(3)
Cd–N(1)–C(1)	163.9(4)	Cd–N(2C)–C(2C)	160.6(4)
Cd–N(3B)–C(3B)	154.1(5)	Cd–N(4)–C(4)	106.8(3)
Cd–N(5)–C(5)	107.3(3)	Cd–N(6)–C(6)	129.4(3)
S(1)–C(1)–N(1)	176.6(4)	S(2)–C(2)–N(2)	176.9(5)
S(3)–C(3)–N(3)	177.1(5)	N(4)–C(4)–C(5)	112.6(4)
N(5)–C(5)–C(4)	111.1(4)	N(6)–C(6)–C(6D)	111.9(5)

*Symmetry codes: A: $1-x, 1-y, -z$; B: $0.5+x, 0.5-y, -0.5+z$; C: $-0.5+x, 0.5-y, 0.5+z$; D: $-x, -y, -z$.

anions, 1,3-μ-SCN$^-$ and 1,1,3-μ_3-SCN$^-$, exist in the complex. The S atom from an 1,1,3-μ_3-SCN$^-$ anion links two Ag(I) atoms with a rather short Ag–Ag distance of 3.133(1) Å [4]. The Ag–S (1,1,3-μ_3-SCN$^-$) distances [average 2.698 Å] are much longer than the Ag–S(1,3-μ-SCN$^-$) distances [average 2.527 Å]. Bond angles around the S atom [Ag–S(1)–C(1) = 104.6°, Ag–S(2)–C(2) = 104.0°] suggest a tetrahedral mode for the S atom in the complex, but the bond angle Ag–S(1)–Ag of 70.92° is much small than expected; it is also smaller than that (110.78°) observed in a 1,1,1,3-μ_4-SCN$^-$ bridging complex of Cu(II) [6]. We believe that both the small Ag–S(1)–Ag angle and short Ag–Ag distance strongly suggest the existence of an Ag–Ag bonding interaction in the multinuclear complex. Cd–N–C angles range from 154.1(5)° to 163.9(4)°. Although the Cd–N(3A)–C(3A) angle of 154.1(5)° implies less overlap between the *sp* hybrid orbital of N(3A) and an orbital of Cd(II), the Cd–N(3A) distance [2.290(4) Å] is significantly shorter than the Cd–N(2A) distance [2.379(4) Å]. This suggests

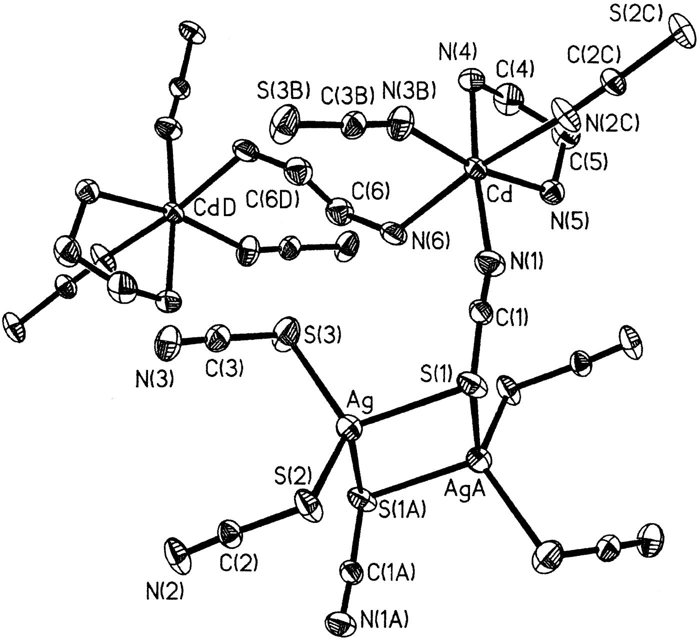

FIGURE 1 Coordination environments around the Cd(II) and Ag(I) atoms showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

the existence of a more electrostatic interaction between the metal and coordinated atoms as reported previously [12]. C–N distances (average 1.135 Å), C–S distances (average 1.649 Å) and S–C–N angles (average 176.9°) in the SCN^- groups show a normal structure for thiocyanate in the complex.

Infrared Spectrum

The peak at 3345 cm^{-1} was assigned to the stretching vibration of the amine group in the complex. Compared with the 3400 cm^{-1} band assigned to the amine group of the free en molecule [10], the 55 cm^{-1} shift strongly suggests coordination of the amine group in the complex. It is a well-established criterion of infrared spectroscopy that ν_{as} (NCS) < 2000 cm^{-1} characterizes an NCS^- anion with a μ-N bridge mode, while ν_{as} (NCS) $\geq$ 2100 cm^{-1} indicates an NCS^- bridge with a 1,3-μ or 1,1,3-μ_3 mode [11]. A strong ν_{as} (NCS) absorption at 2098 cm^{-1} in the complex shows the coordination of SCN^- with a 1,3-μ or 1,1,3-μ_3 bridge mode and agrees well with the molecular structure.

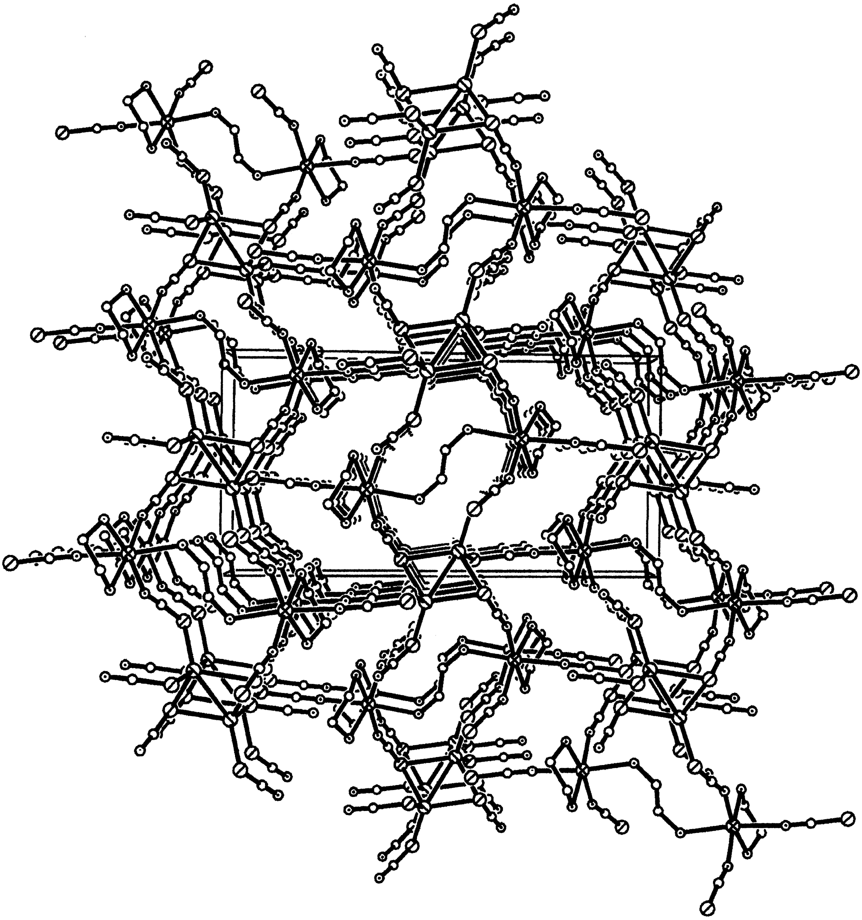

FIGURE 2 Packing diagram of the polymeric complex viewed along the *a* axis.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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