

Adducts of Cadmium Diethyldithiocarbamate with Bidentate Nitrogen Ligands

CLAUDIO AIROLDI, SEVERINO F. DE OLIVEIRA

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081 Campinas, SP (Brazil)

SILVANA G. RUGGIERO

Departamento de Química, Universidade Federal de Uberlândia, 38400 Uberlândia, MG (Brazil)

and JOHANNES R. LECHAT*

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560 São Carlos, SP (Brazil)

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Abstract

Reactions of $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ with 1,10-phenanthroline or 2,2'-bipyridine produce crystalline 1:1 adducts. Thermogravimetric studies show that the 2,2'-bipyridine adduct initiates decomposition by loss of the neutral ligand whereas the 1,10-phenanthroline adduct undergoes a more complex decomposition. The crystal structure of the adducts show their monomeric nature with hexacoordination of the metal in a distorted octahedral geometry.

Introduction

Cadmium dialkyldithiocarbamates and their derivatives are known as efficient therapeutic chelating agents [1]. Several analytical applications of these compounds have been extensively described [2]. Although not commercially important, they are also known for accelerating the vulcanization of 'diene' rubbers [3]. We report herein the preparation and crystal structure determination of [(1,10-phenanthroline) cadmium bis(*N,N*-diethyldithiocarbamate)] (**I**) and [(2,2'-bipyridine) cadmium bis(*N,N*-diethyldithiocarbamate)] (**II**). The structures of similar adducts involving the complexes of cadmium with other dithioacids, for instance [(1,10-phenanthroline) cadmium bis(*O*-ethylxanthate)] [4] and [(2,2'-bipyridine) cadmium bis(*S*-butylthioxanthate)] [5] have been previously reported. Cadmium in both adducts is hexacoordinated by four sulphur atoms from the xanthate or thioxanthate ligand and two nitrogen atoms from the neutral ligand. In contrast, a dimeric centrosymmetric structure is found for cadmium bis(*N,N*-diethyldithiocarbamate) [6] and cadmium bis(*N,N*-hexamethylenedithiocarbamate)

[7] and a dimeric twofold symmetric structure is found for cadmium bis(*N,N*-dibutyldithiocarbamate) [8] where cadmium is essentially tetracoordinated by sulphur atoms, a fifth longer contact being observed owing to the binuclear nature of the complexes.

Results and Discussion

Cadmium diethyldithiocarbamate, $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ dissolved in a 1:1 mixture of ethanol and chloroform reacts with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) in ethanol in a 1:1 and 1:1.2 molar ratio, respectively forming crystalline adducts which were isolated.

The analytical data of these compounds are presented in Table 1 and are in good agreement with the expected values.

The mode of coordination of the chelates mainly affects the C–N and C–S stretching bands [9]. Diethyldithiocarbamate anion has C–N stretching frequencies at 1460 and 1465 cm^{-1} in its sodium and diethylammonium salts, respectively. The shift of

TABLE 1. Elemental analysis and melting points of the cadmium compounds

Compound	Analysis: found (calc.) (%)			Melting point (°C)
	C	H	N	
$\text{Cd}(\text{S}_2\text{CNEt}_2)_2$	30.0 (29.4)	4.7 (4.9)	6.6 (6.9)	249–250
[(phen) $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$]	45.6 (44.9)	4.6 (4.8)	9.3 (9.5)	278–280
[(bipy) $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$]	42.1 (42.5)	4.9 (5.0)	10.0 (9.9)	204–205

* Author to whom correspondence should be addressed.

the C–N stretching bands to 1500 cm^{-1} for both adducts indicates an increase of the double bond character of this bond due to the release of electron density of the nitrogen atom of the NEt_2 groups which results in high density on the sulphur atoms via the π system [10]. The strong band around 1000 cm^{-1} for such chelates has been assigned to the stretching of the C–S groups and associated to the bidenticity of the ligand [11]. This band is splitted in a doublet, at 1085 and 1105 cm^{-1} in the adducts, and this fact has been related to the interligand coupling of the C–S modes of vibration of the coordinated ligands [12]. However an earlier explanation of this splitting, attributing it to the coordination of the metal by two sulphur atoms in an anisobidentate way [13, 14] seems to be more adequate since, as will be shown below, the Cd–S bond lengths are significantly different. The same behaviour of the C–N and C–S vibration frequencies was observed for the *o*-phenanthroline and bipyridine adducts, indicating thus that those bands are not altered by the presence of the additional ligand.

The thermal behaviour of $\text{Cd}(\text{S}_2\text{CNET}_2)_2$ and $[(\text{phen})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$ is similar. Both initiate decomposition in the same temperature range, $250\text{ }^\circ\text{C}$

for the complex and $225\text{ }^\circ\text{C}$ for the adduct. Both compounds lose mass upto $345\text{ }^\circ\text{C}$, leaving residues of 15 and 9%, respectively. In the case of $[(\text{bipy})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$ a mass loss of 27.5% is observed between 125 and $205\text{ }^\circ\text{C}$ which corresponds closely to that required for 2,2'-bipyridine (27.6%). The compound continues losing mass until $325\text{ }^\circ\text{C}$, leaving a residue of 17%. As already observed with similar zinc adducts [15] the phenanthroline adduct behaves differently from the bipyridine adduct.

The structure of $[(\text{phen})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$ contains four discrete monomeric units per unit cell, i.e. two independent molecules per asymmetric unit (Fig. 1). Selected bond distances and angles are listed in Table 2.

The structure of $[(\text{bipy})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$ contains four discrete monomeric units per unit cell, i.e. the molecule lies on a twofold crystallographic axis, one half of it constituting the asymmetric unit as frequently occurs with this kind of compounds [4, 5] (Fig. 2). Selected bond distances and angles are listed in Table 3.

TABLE 2. Selected bond lengths (Å) and angles ($^\circ$) with e.s.d.s in parentheses for $[(\text{phen})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$

Distances (Å)			
Molecule I		Molecule I'	
Cd–S(1)	2.595(4)	Cd'–S(1')	2.635(3)
Cd–S(2)	2.745(4)	Cd'–S(2')	2.667(4)
Cd–S(3)	2.610(4)	Cd'–S(3')	2.627(4)
Cd–S(4)	2.717(3)	Cd'–S(4')	2.766(4)
Cd–N(3)	2.42(1)	Cd'–N(3')	2.39(2)
Cd–N(4)	2.384(9)	Cd'–N(4')	2.428(8)
S(1)–C(1)	1.70(1)	S(1')–C(1')	1.71(1)
S(2)–C(1)	1.71(1)	S(2')–C(1')	1.72(2)
N(1)–C(1)	1.36(2)	N(1')–C(1')	1.36(2)
S(3)–C(6)	1.72(1)	S(3')–C(6')	1.71(1)
S(4)–C(6)	1.72(1)	S(4')–C(6')	1.73(1)
N(2)–C(6)	1.35(2)	N(2')–C(6')	1.32(2)
Angles ($^\circ$)			
S(1)–Cd–S(2)	67.3(1)	S(1')–Cd'–S(2')	68.4(2)
S(1)–Cd–S(3)	116.9(1)	S(1')–Cd'–S(3')	154.9(2)
S(1)–Cd–S(4)	101.9(1)	S(1')–Cd'–S(4')	94.1(2)
S(1)–Cd–N(3)	99.7(3)	S(1')–Cd'–N(3')	91.8(2)
S(1)–Cd–N(4)	140.6(3)	S(1')–Cd'–N(4')	118.9(2)
S(2)–Cd–S(3)	96.4(1)	S(2')–Cd'–S(3')	107.2(1)
S(2)–Cd–S(4)	154.6(1)	S(2')–Cd'–S(4')	121.2(2)
S(2)–Cd–N(3)	120.6(2)	S(2')–Cd'–N(3')	139.1(3)
S(2)–Cd–N(4)	86.9(3)	S(2')–Cd'–N(4')	90.0(3)
S(3)–Cd–S(4)	67.1(1)	S(3')–Cd'–S(4')	66.4(1)
S(3)–Cd–N(3)	136.2(3)	S(3')–Cd'–N(3')	104.9(2)
S(3)–Cd–N(4)	94.3(3)	S(3')–Cd'–N(4')	85.3(2)
S(4)–Cd–N(3)	83.1(2)	S(4')–Cd'–N(3')	94.8(2)
S(4)–Cd–N(4)	112.6(3)	S(4')–Cd'–N(4')	142.3(3)
N(3)–Cd–N(4)	67.6(3)	N(3')–Cd'–N(4')	68.0(4)

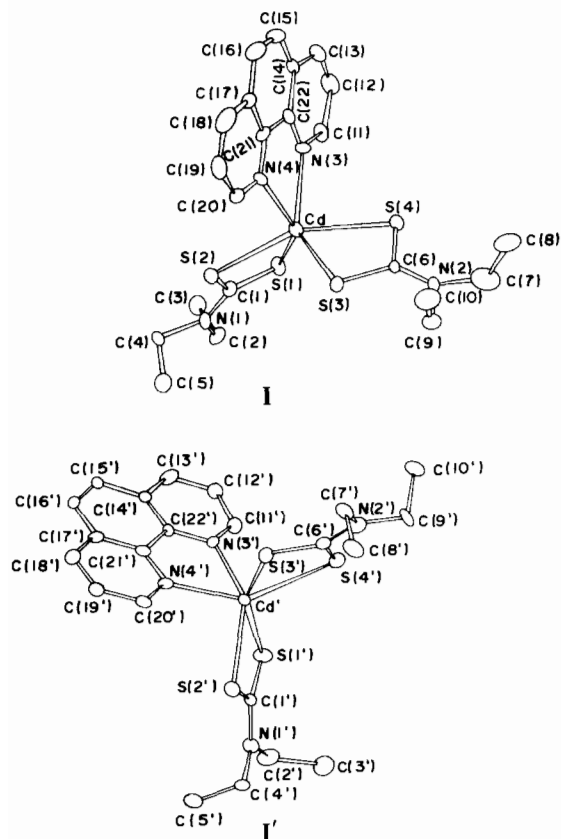


Fig. 1. Representation of the independent molecules of $[(\text{phen})\text{Cd}(\text{S}_2\text{CNET}_2)_2]$ giving atomic numbering.

The cadmium atom in both structures is hexacoordinated by four sulphur atoms from the chelating dithiocarbamate groups and two nitrogen atoms from the chelating phenanthroline in **I** or bipyridine in **II**. Selected molecular parameters for related cadmium

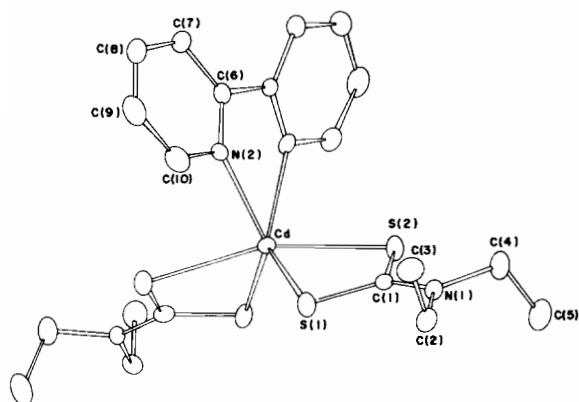


Fig. 2. Representation of $[(bipy)Cd(S_2CNEt_2)_2]$ giving atomic numbering of the asymmetric unit.

TABLE 3. Selected bond lengths (Å) and angles ($^\circ$) with e.s.d.s in parentheses for $[(bipy)Cd(S_2CNEt_2)_2]^a$

Distances (Å)			
Cd–S(1)	2.683(1)	S(1)–C(1)	1.720(4)
Cd–S(2)	2.651(1)	S(2)–C(1)	1.717(4)
Cd–N(2)	2.430(3)	N(1)–C(1)	1.329(5)
Angles ($^\circ$)			
S(1)–Cd–S(2)	67.33(3)	S(2)–Cd–S(2')	162.33(4)
S(1)–Cd–S(1')	121.61(3)	S(2)–Cd–N(2)	83.47(8)
S(1)–Cd–S(2')	103.59(3)	S(2)–Cd–N(2')	111.66(8)
S(1)–Cd–N(2)	137.38(7)	N(2)–Cd–N(2')	67.61(8)
S(1)–Cd–N(2')	94.29(7)		

^aPrimed and unprimed labelled atoms are related by twofold symmetry.

TABLE 4. Comparative molecular parameters for related cadmium compounds

Compound formula	Coordination number	S–Cd–S ($^\circ$)	S–C–S ($^\circ$)	Cd–S ^e (Å)	C–S (Å)	S ₂ C–N (Å)	Reference
Cd(S ₂ CNEt ₂) ₂	4 ^a	70.9(1) ^d	120.2(7) ^d	2.580	1.720	1.33(2) ^d	6
Cd(S ₂ CNC ₆ H ₁₂) ₂	4 ^b	70.0(4) ^d	120.5(18) ^d	2.582	1.71	1.33(4) ^d	7
Cd(S ₂ CNBu ₂) ₂	4 ^c	70.2(2) ^d	119(1) ^d	2.563	1.71	1.36(3) ^d	8
[(phen)Cd(S ₂ COEt) ₂]	6	67.1(1)	123.1(6)	2.687	1.69		4
[(bipy)Cd(S ₂ CSBu) ₂]	6	66.9(1)	123.8(2)	2.684	1.678		5
[(bipy)Cd(S ₂ CNEt ₂) ₂]	6	67.36(3)	118.8(3)	2.667	1.719	1.329(5)	this work
[(phen)Cd(S ₂ CNEt ₂) ₂]	6	67.3(1)	121.3(8)	2.670	1.72	1.36(2)	this work
		67.1(1)	118.4(7)			1.35(2)	
		68.4(2)	120.7(7)			1.36(2)	
		66.4(1)	118.5(8)			1.32(2)	

^aAdditional Cd–S at 2.800(3) Å.

^bAdditional Cd–S at 2.873(10) Å.

^cAdditional Cd–S at 2.888(5) Å.

^dBond angle or

distance for bidentately bonded ligands only.

^eMean bond length, excluding additional bond, when present.

compounds are given in Table 4. The acceptance of an additional neutral ligand causes an increase of the Cd–S bond lengths and a consequent lowering of the S–Cd–S bite angle of the anionic ligand. As long as the dithiocarbamate derivatives are considered, no significant alterations of the C–N and mean C–S bond lengths or of the S–C–S angles are observed. In all cases the dithiocarbamate ligands are asymmetrically linked to cadmium and the sulphur atom engaged in the shortest bond to the carbon atom also makes the shortest link to the cadmium atom.

Selected molecular parameters concerning the link of the bidentate nitrogen ligand to the cadmium atom are presented in Table 5. The Cd–N bonds are systematically longer in the adducts deriving from cadmium diethyldithiocarbamate than in the two adducts deriving from xanthate or thioxanthate. The stronger interaction of the neutral ligand with cadmium occurs in those compounds at the expenses of the interactions of the anionic ligand with cadmium, since they present the longest Cd–S bonds.

A structure similar to the structures of **I** and **II** is observed in the case of [(1,10-phenanthroline)zinc bis(dibutyldithiocarbamate)] [15]. It is however to be noted that contrarily to what happens in the case of the Cd compounds, the dithiocarbamate ligand links symmetrically to Zn since the difference between the reported Zn–S bond lengths is not statistically significant.

Experimental

Thermogravimetric curves were obtained in a dynamic atmosphere of nitrogen in the range 30–700 $^\circ$ C, using a Du Pont model 1090 instrument with a programmed heating rate of 10 $^\circ$ C min⁻¹. The melting points of the compounds were measured by a Reichert Termopan ultramicroscope with a programmed heating rate of 3 $^\circ$ C min⁻¹. Infrared spectra

TABLE 5. Comparative molecular parameters involving the bidentate nitrogen ligand for related cadmium compounds

Compound formula	N—Cd—N (°)	Cd—N (Å)
[(phen)Cd(S ₂ COEt) ₂]	69.5(3)	2.386(8)
[(bipy)Cd(S ₂ CSBu) ₂]	69.0(1)	2.363(3)
[(bipy)Cd(S ₂ CNEt ₂) ₂]	67.61(8)	2.430(3)
[(phen)Cd(S ₂ CNEt ₂) ₂]	67.6(3)	2.42(1)
	68.0(4)	2.384(9)
		2.39(2)
		2.428(8)

were obtained for sample mulls in Fluorolube and KBr discs on a Perkin-Elmer 339B spectrophotometer.

Reagent

Cadmium bis(diethyldithiocarbamate), Cd(S₂CNEt₂)₂: an ethanolic solution of sodium diethyldithiocarbamate (0.10 mol) prepared as previously described [16] was slowly added to an ethanolic solution of cadmium chloride (0.05 mol). A white

precipitate was produced immediately, collected by suction, washed with water and dried *in vacuo*. The solid was recrystallized from a 1:1 mixture of ethanol and chloroform.

Preparation of the Adducts

[[1,10-Phenanthroline) cadmium bis(diethyldithiocarbamate)] [(phen)Cd(S₂CNEt₂)₂]

An ethanolic solution of 1,10-phenanthroline monohydrate (5.0×10^{-4} mol) was slowly added to Cd(S₂CNEt₂)₂ (5.0×10^{-4} mol) dissolved in a 1:1 mixture of ethanol and chloroform. A solid appeared immediately which was left with the solution for 24 h before being collected, dried and recrystallized from hot chloroform.

[[2,2'-Bipyridine) cadmium bis(diethyldithiocarbamate)] [(bipy)Cd(S₂CNEt₂)₂]

This adduct was prepared as the previous one by using 6.3×10^{-4} mol of bipyridine and 5.3×10^{-4} mol of Cd(S₂CNEt₂)₂.

Analytical data and melting points are reported in Table 1.

TABLE 6. Crystal and details of intensity data measurement and least-squares refinement for I and II

	I	II
Molecular formula	CdS ₄ N ₄ C ₂₂ H ₂₈	CdS ₄ N ₄ C ₂₀ H ₂₈
M_r	589.15	565.13
Crystal system	triclinic	monoclinic
Cell parameters		
a (Å)	11.042(2)	18.118(2)
b (Å)	15.185(2)	8.396(1)
c (Å)	16.978(3)	16.941(2)
α (°)	106.43(1)	90
β (°)	99.84(1)	105.84(1)
γ (°)	101.35(1)	90
Cell volume (Å ³)	2598(2)	2479(1)
Space group	$P\bar{1}$	$C2/c$
Z	4	4
D_c (Mg m ⁻³)	1.506	1.514
μ (Mo K α) (mm ⁻¹)	1.162	1.215
Crystal size (mm)	0.13 \times 0.33 \times 0.40	0.15 \times 0.25 \times 0.40
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.527	0.595
Interval h, k, l	0 \rightarrow 11, -15 \rightarrow 15, -17 \rightarrow 17	-21 \rightarrow 20, 0 \rightarrow 9, 0 \rightarrow 20
Max. and min. transmission factors	0.858, 0.692	0.852, 0.719
No. reflections measured	6633	2427
No. unique reflections	6365	2174
No. observed reflections [$I > 3\sigma(I)$]	5220	1849
R_{int}	0.016	0.024
Weighting scheme parameter (p)	0.00316	0.00053
R, R_w	0.059, 0.078	0.030, 0.033
Goodness of fit (s)	1.25	1.17
($\Delta\rho$) _{max}	0.92	0.52
($\Delta\rho$) _{min}	-0.61	-0.50
$\Delta/e.s.d.$	0.05	0.02
	(0.38 U of terminal C atoms)	

TABLE 7. Fractional atomic coordinates for [(phen)Cd(S₂CNEt₂)₂] and equivalent isotropic temperature factors with e.s.d.s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²)
Cd	0.54916(8)	0.50923(6)	0.25217(5)	3.23(2)	Cd'	-0.01085(8)	-0.00398(6)	0.76229(5)	3.11(2)
S(1)	0.7841(3)	0.5013(2)	0.2877(2)	4.13(8)	S(1')	0.2133(3)	0.0375(2)	0.8672(2)	4.30(8)
S(2)	0.5723(3)	0.3262(2)	0.2135(2)	4.02(8)	S(2')	-0.0184(3)	-0.0958(2)	0.8748(2)	3.34(7)
S(3)	0.4218(4)	0.5014(2)	0.3672(2)	4.72(9)	S(3')	-0.2412(3)	0.0140(2)	0.7143(2)	4.01(8)
S(4)	0.5606(3)	0.6836(2)	0.3586(2)	4.36(8)	S(4')	-0.0245(3)	0.1829(2)	0.8030(2)	4.46(8)
N(1)	0.8140(9)	0.3295(7)	0.2699(6)	3.8(2)	N(1')	0.2079(9)	-0.0484(6)	0.9833(6)	3.2(2)
N(2)	0.436(1)	0.6672(7)	0.4792(7)	5.0(3)	N(2')	-0.265(1)	0.1901(7)	0.7633(7)	4.4(3)
C(1)	0.730(1)	0.3818(8)	0.2580(7)	3.1(3)	C(1')	0.139(1)	-0.0350(7)	0.9152(6)	2.9(3)
C(2)	0.950(1)	0.372(1)	0.3128(8)	4.6(3)	C(2')	0.343(1)	0.002(1)	1.0207(9)	5.3(4)
C(3)	1.030(1)	0.379(1)	0.251(1)	5.5(4)	C(3')	0.358(2)	0.093(1)	1.091(1)	8.0(6)
C(4)	0.773(1)	0.2225(8)	0.2378(8)	3.8(3)	C(4')	0.152(1)	-0.1112(8)	1.0283(7)	3.7(3)
C(5)	0.726(1)	0.182(1)	0.3030(9)	5.4(4)	C(5')	0.179(1)	-0.2080(9)	0.9958(8)	4.7(4)
C(6)	0.470(1)	0.6227(8)	0.4087(7)	3.4(3)	C(6')	-0.186(1)	0.1350(8)	0.7591(7)	3.6(3)
C(7)	0.509(2)	0.778(1)	0.533(1)	8.3(5)	C(7')	-0.401(1)	0.1489(9)	0.7288(9)	5.3(4)
C(8)	0.426(2)	0.825(2)	0.506(1)	10.9(7)	C(8')	-0.471(1)	0.119(1)	0.791(1)	6.6(4)
C(9)	0.357(1)	0.6160(9)	0.5227(8)	5.4(4)	C(9')	-0.223(1)	0.2929(8)	0.8067(9)	5.5(4)
C(10)	0.219(2)	0.598(1)	0.488(1)	7.4(5)	C(10')	-0.192(2)	0.350(1)	0.747(1)	7.1(4)
N(3)	0.5597(9)	0.5923(7)	0.1504(6)	3.8(2)	N(3')	0.0841(9)	-0.0001(6)	0.6462(6)	3.2(2)
N(4)	0.3643(9)	0.4497(7)	0.1377(6)	3.9(2)	N(4')	-0.0826(8)	-0.1550(6)	0.6480(5)	3.0(2)
C(11)	0.665(1)	0.663(1)	0.156(1)	5.1(4)	C(11')	0.174(1)	0.0734(9)	0.6468(8)	4.0(3)
C(12)	0.656(1)	0.7171(9)	0.1004(9)	5.5(4)	C(12')	0.228(1)	0.0745(9)	0.5781(8)	4.5(3)
C(13)	0.550(1)	0.6977(9)	0.0403(9)	5.8(4)	C(13')	0.194(1)	-0.005(1)	0.5084(8)	4.4(3)
C(14)	0.445(1)	0.6214(8)	0.0297(7)	4.6(3)	C(14')	0.102(1)	-0.0869(8)	0.5062(7)	3.2(3)
C(15)	0.328(2)	0.594(1)	-0.0344(8)	6.4(4)	C(15')	0.062(1)	-0.1706(9)	0.4335(8)	4.5(3)
C(16)	0.232(1)	0.521(1)	-0.0420(9)	6.7(5)	C(16')	-0.024(1)	-0.2470(8)	0.4347(8)	4.2(3)
C(17)	0.240(1)	0.4703(9)	0.0179(8)	5.0(3)	C(17')	-0.078(1)	-0.2441(8)	0.5061(7)	3.5(3)
C(18)	0.144(1)	0.391(1)	0.011(1)	6.8(5)	C(18')	-0.172(1)	-0.3218(8)	0.5073(8)	4.0(3)
C(19)	0.164(1)	0.340(1)	0.067(1)	6.1(4)	C(19')	-0.218(1)	-0.3124(8)	0.5789(8)	4.2(3)
C(20)	0.273(1)	0.3728(9)	0.1295(9)	4.4(3)	C(20')	-0.174(1)	-0.2300(7)	0.6483(7)	3.2(3)
C(21)	0.352(1)	0.4946(8)	0.0811(7)	3.4(3)	C(21')	-0.040(1)	-0.1618(7)	0.5780(6)	2.7(2)
C(22)	0.454(1)	0.5731(8)	0.0890(7)	3.5(3)	C(22')	0.053(1)	-0.0799(7)	0.5773(7)	2.7(2)

TABLE 8. Fractional atomic coordinates for [(bipy)Cd(S₂CNEt₂)₂] and equivalent isotropic temperature factors with e.s.d.s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} (Å ²)
Cd	0	0.19425(4)	0.75	2.88(1)
S(1)	0.13355(5)	0.0384(1)	0.80400(5)	3.55(3)
S(2)	0.06887(5)	0.1458(1)	0.63270(6)	3.91(3)
C(1)	0.1442(2)	0.0674(4)	0.7072(2)	2.80(9)
N(1)	0.2098(2)	0.0311(3)	0.6907(2)	3.22(8)
C(2)	0.2750(2)	-0.0403(5)	0.7517(2)	3.8(1)
C(3)	0.3279(2)	0.0820(6)	0.8023(3)	4.7(1)
C(4)	0.2230(2)	0.0688(6)	0.6105(2)	4.7(1)
C(5)	0.2018(3)	-0.0646(7)	0.5509(3)	6.8(2)
N(2)	-0.0463(2)	0.4347(3)	0.6725(2)	3.23(8)
C(6)	-0.0185(2)	0.5738(4)	0.7053(2)	2.92(9)
C(7)	-0.0223(2)	0.7123(5)	0.6582(2)	4.0(1)
C(8)	-0.0557(3)	0.7043(6)	0.5754(3)	5.0(1)
C(9)	-0.0852(3)	0.5613(6)	0.5418(2)	5.5(2)
C(10)	-0.0796(2)	0.4296(5)	0.5914(2)	4.5(1)

Crystallographic Studies

A crystal of suitable size was mounted on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K α radiation. Cell parameters were refined by least-squares on setting angles from 25 reflections. Data were collected using ω - 2θ scans, corrected for Lorentz, polarization and absorption (based on crystal-face measurements), maximum scan speed = 5.0° min⁻¹, structure solved by Patterson and Fourier methods. Complex neutral-atom scattering factors [17]. Full-matrix least-squares refinement via SHELX-76 [18], function minimized: $\sum w(|F_o| - |F_c|)^2$ with $w = (\sigma(F_o)^2 + pF_o^2)^{-1}$. All calculations were performed on a VAX 11/780 computer. Crystal data and the details of intensity data measurement and least-squares refinement are given in Table 6. Final atomic parameters for the structure of [1,10-phenanthroline) cadmium bis(diethylthiocarbamate)] are listed in Table 7, while those corresponding to [(2,2'-bipyridine) cadmium bis(diethylthiocarbamate)] are listed in Table 8.

Supplementary Material

Thermal parameters, H atom coordinates and observed and calculated structure factors are available from the authors on request.

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