Octahedrally Co-ordinated Zinc and Cadmium Compounds with Five-membered Heterocyclic OS_3N_2 Ligands †

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The compounds $[M(OS_3N_2)_6][AsF_6]_2$ (M = Zn or Cd) have been prepared in which the metal atoms are co-ordinated by six five-membered heterocyclic ligands. The molecular and crystal structures were determined by *X*-ray analysis. The metal is bonded to each ligand *via* the exocyclic oxygen atom, giving a slightly distorted octahedral environment. The S_3N_2 rings have an envelope conformation where the S atom connected to the oxygen is out of the plane formed by the other four atoms. The AsF_6^- group is slightly disordered in the cadmium compound, considerably disordered in the zinc compound.

The stereochemistry of Zn^{2+} and Cd^{2+} ions is determined solely by size and by electrostatic and covalent bonding forces, because ligand-field stabilization effects are absent due to their completed *d* shells. Therefore the co-ordination number of six for Zn^{2+} is rare.[1] We report herein a new class of co-ordination compounds with envelope-shaped heterocyclic OS_3N_2 ligands in which the oxygen is bonded in an exocyclic manner to a sulphur atom. Such a ligand may co-ordinate to the metal *via* sulphur, nitrogen, or oxygen. The molecular structures of $[M(OS_3N_2)_6][AsF_6]_2$ (M = Zn or Cd) were determined by *X*-ray diffraction analysis.

Experimental

The reaction of zinc or cadmium metal with excess of arsenic pentafluoride in liquid sulphur dioxide leads to the formation of the adduct of zinc bis[hexafluoroarsenate(V)] or the corresponding cadmium salt with sulphur dioxide [equation (i), M = Zn or Cd].[2] The content of SO_2 in compound (1)

$$\underset{}{M + 3\ AsF_5} \xrightarrow{SO_2} \underset{(1)}{[M(SO_2)_x][AsF_6]_2} + AsF_3 \qquad (i)$$

varies from $x = 2$ to 4 depending on the pressure of SO_2. All solvents and apparatus were carefully dried before use. The products were handled under an inert atmosphere of either nitrogen or argon.

*Adduct of Zinc Bis[hexafluoroarsenate(*V*)] or Cadmium Bis[hexafluoroarsenate(*V*)] with Two Sulphur Dioxide Molecules.*—Zinc or cadmium (0.07 mol) was placed in a pressure-flask and at −78 °C AsF_5 (0.22 mol) and SO_2 (15 cm^3) were added. The flask was slowly warmed to room temperature, with stirring. Within 12 h a clear, blue solution resulted. After removal of the solvent under vacuum, a nearly white product resulted {Found: F, 39.8; Zn, 11.5. Calc. for $[Zn(SO_2)_2][AsF_6]_2$: F, 39.9; Zn, 11.4. Found: Cd, 20.2; F, 40.1. Calc. for $[Cd(SO_2)_2][AsF_6]_2$: Cd, 20.5; F, 41.7%}.

*Hexakis(1-oxo-1,2,4-trithiadiazole)-zinc and -cadmium Bis[hexafluoroarsenate(*V*)].*—When compound (1) was treated with excess of OS_3N_2, prepared from $S_3N_2Cl_2$ and formic acid,[3] octahedrally co-ordinated zinc or cadmium salts (2) could be isolated [equation (ii)].

Table 1. Crystal data and structure analysis [a]

	(2a) $[Zn(OS_3N_2)_6]$- $[AsF_6]_2$	(2b) $[Cd(OS_3N_2)_6]$- $[AsF_6]_2$
M	1 284.43	1 331.45
a/Å	8.927(14)	9.046(4)
b/Å	10.058(5)	10.237(14)
c/Å	10.925(9)	11.053(5)
α/°	67.06(5)	65.68(5)
β/°	82.88(9)	80.86(4)
γ/°	88.69(7)	87.38(6)
U/Å³	896(2)	920.7(1.6)
D_c/g cm^{-3}	2.38	2.40
μ(Mo-K_α)/cm^{-1}	37.6	35.6
Crystal dimensions (mm)	0.10 × 0.16 × 0.22	0.20 × 0.25 × 0.35
Total reflections	2 835	3 178
Independent reflections	1 608	2 447
Observed reflections	1 438 [$I > 0.3\sigma(I)$]	2 312 [$I > 0.2\sigma(I)$]
$2\theta_{max}$/°	40	46
R	0.095	0.057
R'	0.078	0.057
S [b]	2.07	2.22

[a] The following are common to both compounds: space group $P\bar{1}$; $Z = 1$. [b] $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{-\frac{1}{2}}$ where NO = number of observations and NV = number of variables.

$$(1) + 6\ OS_3N_2 \longrightarrow [M(OS_3N_2)_6][AsF_6]_2 + x\ SO_2 \qquad (ii)$$
$$(2a;\ M = Zn)$$
$$(2b;\ M = Cd)$$

The zinc or cadmium salt (1) (0.003 mol) was cooled to −78 °C in a pressure-flask, then OS_3N_2 (0.02 mol) and SO_2 (15 cm^3) were added. The flask was allowed to warm to room temperature and stirred for 16 h. After removal of SO_2, the dark orange residue was washed with methylene chloride and recrystallized from SO_2 {Found: F, 18.7; N, 13.0; S, 43.6. Calc. for $[Zn(OS_3N_2)_6][AsF_6]_2$: F, 17.8; N, 13.1; S, 44.9. Found: F, 16.0; N, 11.6; S, 39.5. Calc. for $[Cd(OS_3N_2)_6][AsF_6]_2$: F, 17.1; N, 12.6; S, 43.3%}.

Compounds (2a) and (2b) form yellow crystals, which were purified by recrystallization from SO_2 in quantitative yield: (2a), m.p. 110—115 °C; (2b), decomposes at 55 °C.

Crystallography.—Crystals of (2a) and (2b) were sealed in glass capillaries as both compounds were found to decompose

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† *Supplementary data available* (No. SUP 23655, 20 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Positional parameters for compounds (2a) and (2b)

	$[Zn(OS_3N_2)_6][AsF_6]_2$			$[Cd(OS_3N_2)_6][AsF_6]_2$		
Atom	x	y	z	x	y	z
Zn, Cd	0.0	0.0	0.0	0.0	0.0	0.0
As	0.287 2(3)	0.293 9(2)	0.355 5(2)	0.282 3(1)	0.303 41(9)	0.354 66(8)
S(1)	0.094 9(6)	0.316 6(5)	0.019 3(4)	0.101 2(2)	0.314 8(2)	0.029 6(2)
S(2)	0.255 6(6)	−0.083 9(5)	0.187 4(5)	0.270 6(2)	−0.096 2(2)	0.183 0(2)
S(3)	0.313 6(6)	0.025 9(5)	−0.221 6(4)	0.324 8(2)	0.026 0(2)	−0.237 3(2)
S(4)	0.230 7(6)	−0.119 9(5)	−0.307 6(5)	0.235 4(3)	−0.112 4(2)	−0.316 2(2)
S(5)	0.322 8(6)	0.351 3(5)	−0.089 7(5)	0.325 8(3)	0.359 9(3)	−0.087 9(2)
S(6)	0.107 1(7)	0.430 0(6)	−0.253 2(5)	0.108 9(3)	0.430 8(2)	−0.245 5(2)
S(7)	0.151 0(9)	−0.115 7(6)	0.388 7(5)	0.169 6(4)	−0.112 0(3)	0.380 0(2)
S(8)	0.341 0(7)	−0.327 4(6)	0.387 3(5)	0.352 0(3)	−0.332 2(3)	0.394 0(2)
S(9)	0.337 8(6)	−0.266 7(5)	−0.072 2(5)	0.337 7(3)	−0.265 8(2)	−0.081 8(2)
O(1)	0.054(1)	0.159 4(9)	0.062 0(9)	0.071 5(6)	0.160 1(5)	0.074 3(4)
O(2)	0.133(1)	−0.134 5(10)	0.131 3(9)	0.149 9(6)	−0.153 8(5)	0.140 5(5)
O(3)	0.178(1)	0.071 0(10)	−0.156 3(10)	0.194 0(6)	0.075 9(5)	−0.171 0(5)
N(1)	0.276(2)	0.401(1)	−0.240(1)	0.279 0(8)	0.405 8(7)	−0.237 2(7)
N(2)	0.018(2)	0.405(1)	−0.112(1)	0.022 4(7)	0.402 8(7)	−0.103 3(6)
N(3)	0.216(2)	−0.272(2)	0.467(2)	0.229 0(11)	−0.269 6(9)	0.467 5(7)
N(4)	0.371(2)	−0.205(1)	0.242(1)	0.386 7(8)	−0.223 8(8)	0.243 0(7)
N(5)	0.247(2)	−0.270(2)	−0.186(1)	0.247 2(8)	−0.265 0(7)	−0.190 8(7)
N(6)	0.391(2)	−0.104(1)	−0.109(1)	0.397 4(7)	−0.108 8(7)	−0.124 5(6)
F(1)	0.453(1)	0.348(2)	0.367(2)	0.443 8(8)	0.369 5(9)	0.356 4(8)
F(2)	0.119(2)	0.245(2)	0.331(2)	0.117 4(9)	0.242 9(10)	0.341 5(8)
F(3) [a]	0.354	0.250	0.219	0.337 2(9)	0.299 6(11)	0.209 2(6)
F(4) [a]	0.228	0.457	0.287	0.211 9(10)	0.459 9(8)	0.292 5(10)
F(5) [a]	0.207	0.350	0.473	0.353 4(15)	0.144 0(9)	0.420 5(12)
F(6) [a]	0.332	0.133	0.422	0.227 2(12)	0.296 5(14)	0.501 8(7)
F(3′) [b]	0.398	0.166	0.332			
F(4′) [b]	0.342	0.389	0.193			
F(5′) [b]	0.170	0.416	0.359			
F(6′) [b]	0.229	0.139	0.500			

[a] Population 0.66 in (2a). [b] Population 0.34 in (2a).

in the air. Precession photographs showed a triclinic lattice. The cell constants were refined from 25 reflections [23 for (2b)] centred on an Enraf-Nonius CAD4F diffractometer. Data were collected in two hemispheres of reciprocal space for compound (2a) and in one hemisphere for (2b) with monochromatized Mo-K_α radiation. The reflections were found to have exceptionally broad profiles due to the very poor crystal quality. Consequently the reflections were measured with an ω scan with $\Delta\omega = 4°$. Three standard reflections were repeatedly measured and showed a gradual intensity decrease of 8% for (2a) and 28% for (2b) due to decay of the crystals. The data were renormalized with respect to the control reflections. No absorption corrections were made. The equivalent reflections were averaged, those with $I > 0.3\sigma(I)$ [(2a)] and $I > 0.2\sigma(I)$ [(2b)] being used in the structure analysis.

The structure of compound (2a) was solved by a combination of Patterson and Fourier techniques. The parameters of Zn, As, and S of (2a) were used as starting values for (2b). Both structures were refined by least-square techniques. They were found to be centrosymmetric with the metal atom at the inversion centre, therefore the space group is $P\bar{1}$.

A difference synthesis showed the AsF_6^- group to be rotationally disordered in (2a). Only two fluorine atoms [the axial atoms F(1) and F(2)] were well resolved, while a smeared ring of density was observed in the equatorial plane in which, only with great difficulty, four local maxima could be observed. Consequently, the AsF_6^- octahedron was believed to be rotationally disordered about the F(1)–As–F(2) axis and was described by a split-atom model. In order to avoid correlation problems, the positions of the split F atoms were not refined. Six localized positions for the F atoms were found in the cadmium compound. The final difference Fourier showed, however, two peaks of 1.2 e Å^{-3}, due to some disorder, but was otherwise featureless. A difference Fourier for (2a) did not show any peaks exceeding 1.2 e Å^{-3}. Details of the crystal data and the structure refinement are given in Table 1. The relatively high R values are a result of the poor crystal quality and of the problem in describing the AsF_6 disorder. The better localization in (2b) is reflected by the lower values of the R factors. Positional parameters are given in Table 2, interatomic angles in Table 3. A stereoscopic view of structure (2a) is shown in Figure 1; Figure 2 gives the numbering scheme and the interatomic distances for both compounds.

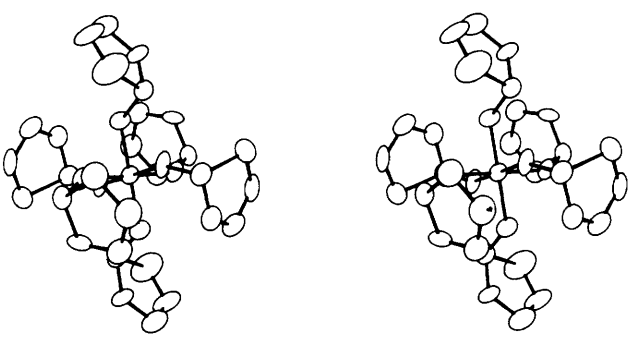

Figure 1. Stereoscopic plot of the structure of compound (2a)

Discussion

The metal atoms are octahedrally co-ordinated by six OS_3N_2 groups, which is an exceptional situation for such large ligands. The Zn–O bonds range from 2.036(8) to 2.093(8) Å.

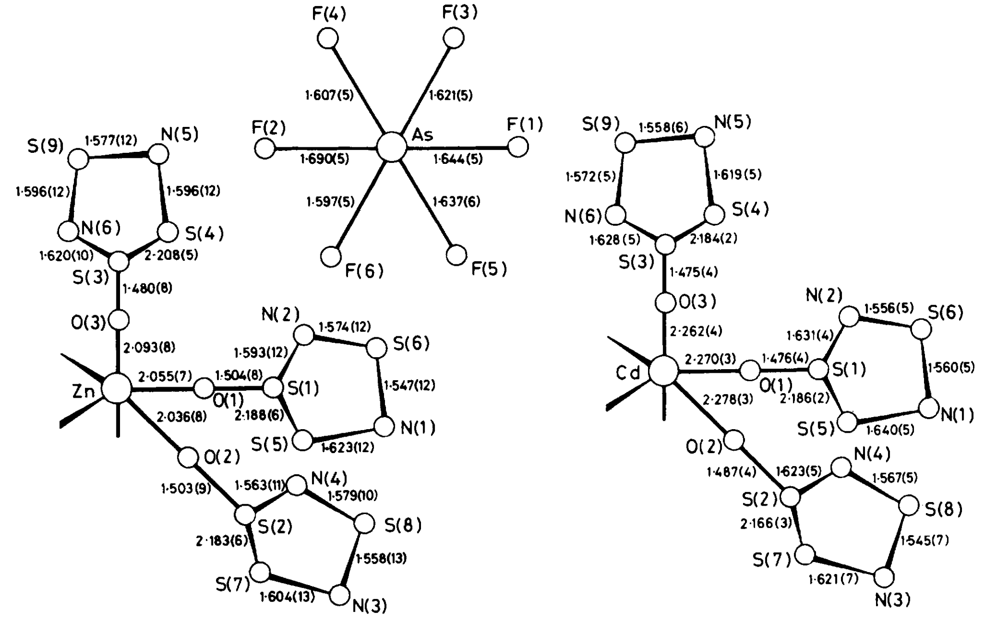

Figure 2. Interatomic distances (Å) in compounds (2a) (left) and (2b) (right). Distances in the AsF_6^- group refer to (2b)

Table 3. Bond angles (°) for compounds (2a) and (2b)

	$[Zn(OS_3N_2)_6][AsF_6]_2$	$[Cd(OS_3N_2)_6][AsF_6]_2$
O(1)-M-O(1)	180.00	180.00
O(1)-M-O(2)	88.2(3), 91.8(3)	84.7(1), 95.3(1)
O(1)-M-O(3)	90.4(3), 89.6(3)	89.6(1), 90.4(1)
O(2)-M-O(2)	180.00	180.00
O(2)-M-O(3)	93.0(3), 87.0(3)	91.2(1), 88.8(1)
O(3)-M-O(3)	180.00	180.00
M-O(1)-S(1)	145.8(5)	141.4(2)
O(1)-S(1)-S(5)	107.0(4)	106.5(2)
O(1)-S(1)-N(2)	108.0(6)	108.7(2)
S(5)-S(1)-N(2)	93.4(5)	92.3(2)
S(1)-S(5)-N(1)	98.1(5)	98.4(2)
S(5)-N(1)-S(6)	115.6(7)	115.5(3)
N(1)-S(6)-N(2)	109.6(7)	109.3(3)
S(6)-N(2)-S(1)	119.1(7)	120.1(3)
M-O(2)-S(2)	124.1(5)	119.8(2)
O(2)-S(2)-S(7)	102.9(4)	102.6(2)
O(2)-S(2)-N(4)	110.9(6)	108.2(3)
S(7)-S(2)-N(4)	92.6(5)	93.4(2)
S(2)-S(7)-N(3)	97.9(5)	97.8(2)
S(7)-N(3)-S(8)	116.9(8)	116.9(4)
N(3)-S(8)-N(4)	106.8(6)	108.7(3)
S(8)-N(4)-S(2)	121.4(8)	119.1(3)
M-O(3)-S(3)	144.7(5)	143.1(2)
O(3)-S(3)-S(4)	106.1(4)	106.0(2)
O(3)-S(3)-N(6)	109.0(5)	109.3(2)
S(4)-S(3)-N(6)	92.9(4)	92.2(2)
S(3)-S(4)-N(5)	98.7(5)	98.6(2)
S(4)-N(5)-S(9)	116.7(7)	116.7(3)
N(5)-S(9)-N(6)	108.6(6)	108.1(3)
S(9)-N(6)-S(3)	119.1(6)	120.2(3)

the Cd-O from 2.262(4) to 2.278(3) Å, and the O-M-O angles range from 87.0(3) to 93.0(3) [(2a)] and 84.7(1) to 95.3(1)° [(2b)]. The deviation from an ideal octahedron is not very large. Distances and angles in the OS_3N_2 groups are rather similar for the six (three for each compound) crystallographically independent groups. The S_3N_2 rings have envelope conformations. The S atom which is connected to O lies about 0.40 Å out of the plane of the remaining ring atoms. The S-N bond distances have intermediate values between single and double bonds. The S-O distance is considerably longer than in compounds with non-complexed SO groups where values between 1.40 and 1.45 Å were observed previously.[4,5] This elongation of the S-O bond corresponds to a lowering of the S=O stretching frequency in compound (2a) by 75 cm^{-1} in comparison to the free ligand (1 125 cm^{-1}), while for (2b) two absorptions at 1 060 and 1 020 cm^{-1} are observed. The overall geometry of the ligands is similar to that found for the adduct of $SnCl_4$ and OS_3N_2.[6]

The $M(OS_3N_2)_6$ unit shows a short intramolecular contact distance of 2.984(9) [(2a)] and 3.038(5) Å [(2b)] between S(2) and O(1). Consequently the M-O(2)-S(2) bond angle is much smaller than the other two M-O-S angles. The F-As-F angles in compound (2b) range from 84.0(3) to 94.9(4)°, indicating an octahedral geometry for AsF_6^- which is believed to exist as well in (2a) although the corresponding angles cannot be derived due to the disorder. The average As-F distances are 1.66 [(2a)] and 1.633 Å [(2b)].

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