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Preparation and Molecular Structure of $Co(NO)_2(S_3N)$

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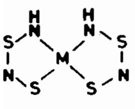
The complex $Co(NO)_2(S_3N)$ (5) is obtained by treating the primary product of the reaction of $Co_2(CO)_8$ and S_4N_4 with gaseous nitric oxide. According to an X-ray structure determination, the cobalt atom is in a pseudo-tetrahedral environment and is part of an almost planar CoS_3N metallocycle.

Introduction

The reaction of tetrasulfur tetranitride, S_4N_4, with metal chlorides MCl_2 (M = Co, Ni, Pd) in alcoholic solution [1–4] – or with H_2PtCl_6 in dimethylformamide [1, 5] – leads to complexes of the types *1–3* containing anionic chelate ligands such as $S_2N_2H^-$ and S_3N^- [19]: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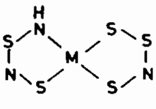
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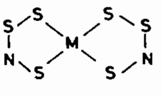
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M = Co	[*cf.* 1]	M = Co	[3]	M = Co	[3]
Ni	[*cf.* 1;2,4,6,7]	Ni	[2–4]	Ni	[2–4]
Pd	[*cf.* 1;6]	Pd	[3]	Pd	[3, 9]
Pt	[*cf.* 1;5,8]	Pt	[5]	Pt	[5]

TABLE I. Mass spectrum[a] of $Co(NO)_2(S_3N)$ (*5*).

m/e	Relative Abundance	Assignment
229	96	$Co(NO)_2(S_3N)^+$
199	100	$Co(NO)(S_3N)^+$
169	65	$Co(S_3N)^+$
123	36	$Co(S_2)^+$
105	42	$Co(SN)^+$
91	37	CoS^+
59	46	Co^+
30	36	NO^+

[a] Varian CH 7, Ionisation energy 70 eV.

X-Ray structural studies involving complexes of type *1* (M = Ni [6, 7], Pd [6], Pt [8]) and *3* (M = Pd [9]) have revealed an almost planar structure in all cases. A binuclear complex of the composition $Pd_2(S_3N)_2(S_3N_2)$ (*4*) is also formed in the reaction of S_4N_4 with $PdCl_2$. In this compound two planar PdS_3N rings are doubly bridged by an S_3N_2 unit [10].

TABLE II. Characteristic IR Frequencies of $Co(NO)_2(S_3N)$ (*5*) and Related Complexes.

Complex	ν(NO) [cm^{-1}]	ν(N–S) [cm^{-1}]	Reference
$Co(NO)_2(S_3N)$ (*5*)	1836, 1778[a]	958, 707[a]	e
$Co(NO)_2(SacSac)$[d]	1827, 1769[b]		13
$Co(NO)_2(S_2PF_2)$	1869, 1797[a]		14
$Ni(S_3N)_2$		984, 720[a]	2, 5
$Pd(S_3N)_2$		1050, 700[a]	12
$Pt(S_3N)_2$		1025, 712[c]	5

[a] Nujol. [b] Hexane. [c] KBr. [d] SacSac = dithioacetylacetonate. [e] This work.

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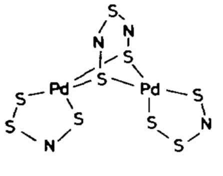
TABLE III. Interatomic Distances (in pm) and Angles (in °) of $Co(NO)_2(S_3N)$ (*5*).

Co–N(1)	166.2(5)	Co–S(1)	224.8(2)
N(1)–O(1)	113.3(7)	S(1)–N(3)	162.9(5)
Co–N(2)	165.3(5)	N(3)–S(2)	155.3(5)
N(2)–O(2)	114.7(7)	S(2)–S(3)	200.2(2)
		Co–S(3)	226.4(2)
S(1)–Co–S(3)	91.80(6)	Co–S(1)–N(3)	109.0(2)
S(1)–Co–N(1)	112.9(2)	S(1)–N(3)–S(2)	124.8(3)
S(1)–Co–N(2)	110.5(2)	N(3)–S(2)–S(3)	110.9(2)
S(3)–Co–N(1)	113.0(2)	S(2)–S(3)–Co	103.54(8)
S(3)–Co–N(2)	114.9(2)	Co–N(1)–O(1)	166.9(5)
N(1)–Co–N(2)	112.1(2)	Co–N(2)–O(2)	164.5(5)



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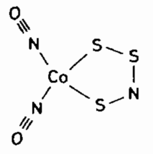

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Results and Discussion

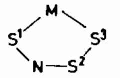
Preparation and Characterization of $Co(NO)_2(S_3N)$ (5)

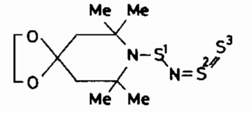
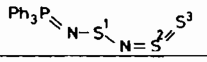
The reaction of $Co_2(CO)_8$ with S_4N_4 results in evolution of CO and formation of an insoluble polymer for which different compositions (*e.g.* CoN_4S_4 [1] or $Co_2(CO)N_4S_4$ [11]) have been found. Treatment of this material with either refluxing diethylether or acetone gives $Co(S_2N_2H)_2$ (*1*, M = Co) [11; *cf.* 1], while nitrosylation of a pentane suspension leads to $Co(NO)_2(S_3N)$ (*5*).

The violet complex *5* sublimes under high vacuum, even at room temperature. The mass spectrum (Table I) shows the molecular ion as well as the fragments expected from successive loss of the two nitrosyl groups and from fragmentation of the S_3N ligand. The IR spectrum contains two ν(NO) stretching absorptions (1836, 1778 cm^{-1}) in the range characteristic for pseudotetrahedral dinitrosylcobalt compounds.

Two absorptions at 958 and 707 cm^{-1} can be assigned to S–N stretching modes [12], although they might be strongly coupled with other vibrations of the CoS_3N ring system. In Table II these character-

TABLE IV. Bond Lengths (in pm) and Angles (in °) of MS_3N Metallocycles and Related Open-chain Compounds



Compound	S(1)–N	N–S(2)	S(2)–S(3)	M–S(3)	M–S(1)	Ref.
$Co(NO)_2(S_3N)$ (*5*)	162.9(5)	155.3(5)	200.2(2)	226.4(2)	224.8(2)	This work
$Pd(S_3N)_2$ (*3*, M = Pd)	169	148	196	229	226	[9]
	165	158	193	226	225	
$Pd_2(S_3N)_2(S_3N_2)$ (*4*)	177.2(15)	147.8(15)	195.9(8)	228.3(5)	227.7(4)	[10]
	174.7(16)	147.0(16)	199.3(9)	228.9(5)	227.9(5)	
For comparison:						
	165.7(6)	156.9(7)	191.2(3)			[17]
	158.7(4)	159.2(4)	190.8(2)			[18]

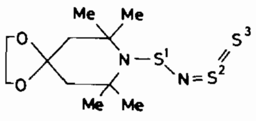
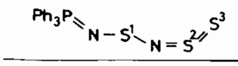
Compound	M–S(1)–N	S(1)–N–S(2)	N–S(2)–S(3)	S(2)–S(3)–M	S(3)–M–S(1)	Ref.
$Co(NO)_2(S_3N)$ (*5*)	109.0(2)	124.8(3)	110.9(2)	103.54(8)	91.80(6)	This work
$Pd(S_3N)_2$ (*3*, M = Pd)	106.6	126.1	112.4	103.1	91.3	[9]
	108.2	123.4	111.9	104.9	91.5	
$Pd_2(S_3N)_2(S_3N_2)$ (*4*)	106.1(4)	122.0(8)	116.3(6)	102.9(3)	92.6(2)	[10]
	105.5(5)	123.9(8)	115.2(7)	101.8(3)	93.1(2)	
For comparison:						
		119.2(4)	114.9(1)			[17]
		120.9	111.4(2)			[18]

TABLE V. Final Atomic Coordinates and Thermal Parameters with their e.s.d's of Co(NO)$_2$(S$_3$N) (*5*). The Anisotropic Temperature Factor is of the Form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$, B_{ij} in 10^4 pm^2

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.1532(1)	0.11850(5)	0.05249(9)	3.44(3)	3.53(3)	3.65(3)	0.20(3)	0.76(3)	−0.04(3)
S(1)	0.2857(3)	0.25580(9)	0.0806(2)	3.59(7)	4.44(7)	5.27(8)	−0.85(6)	0.97(6)	−0.55(6)
N(3)	0.0764(8)	0.3237(3)	0.0366(6)	5.4(3)	3.8(2)	4.2(2)	−0.4(2)	1.6(2)	−0.1(2)
S(2)	−0.1731(3)	0.29648(9)	−0.0147(2)	4.34(8)	3.96(7)	4.45(7)	0.64(5)	1.32(6)	0.37(5)
S(3)	−0.2042(2)	0.16634(9)	−0.0208(2)	3.20(6)	3.98(7)	6.04(8)	−0.34(6)	0.72(6)	0.15(6)
N(1)	0.2168(9)	0.0632(3)	0.2525(6)	5.0(3)	4.6(2)	4.2(2)	0.7(2)	1.1(2)	−0.1(2)
O(1)	0.2749(9)	0.0140(3)	0.3689(7)	10.1(4)	6.5(3)	4.8(2)	3.0(3)	1.1(2)	1.4(2)
N(2)	0.2336(8)	0.0669(3)	−0.1182(6)	4.6(3)	4.1(2)	4.4(2)	0.5(2)	1.3(2)	0.1(2)
O(2)	−0.3161(8)	−0.0202(3)	0.2038(6)	7.4(3)	5.7(2)	5.7(2)	2.1(2)	2.4(2)	0.3(2)

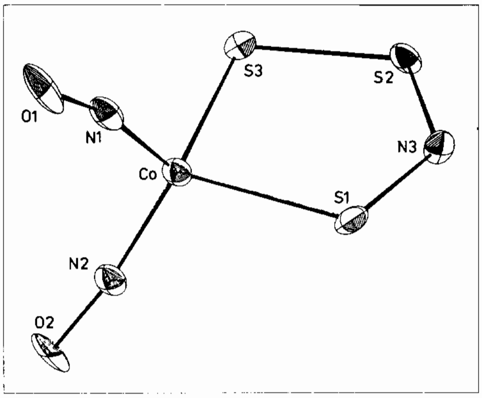


Fig. 1. A perspective drawing of Co(NO)$_2$(S$_3$N) (*5*).

istic IR absorptions of *5* are compared with those of related complexes containing either a Co(NO)$_2$ fragment combined with an anionic dithio chelate ligand, or chelating S$_3$N ligands coordinated to other metals. However, the unequivocal proof of the molecular structure is based on an X-ray crystallographic study of *5*.

Molecular Structure of Co(NO)$_2$(S$_3$N) (5)

Bond lengths and angles within the five-membered metallocycle of Co(NO)$_2$(S$_3$N) (*5*) (Table III) are in close agreement with those found in the palladium complexes Pd(S$_3$N)$_2$ (*3*, M = Pd) [9] and Pd$_2$(S$_3$N)$_2$(S$_3$N$_2$) (*4*) [10]. There is also a surprising similarity with open-chain compounds containing the –S–N=S=S unit (see Table IV). Complex *5* contains a nearly planar metallocycle, only the sulfur atom S(1) deviates slightly (by 9(1) pm) from the plane formed by the other atoms of the ring which are exactly coplanar.

The Co–N and N–O bond lengths are within the range found for other tetrahedral dinitrosylmetal complexes [*cf.* 16]. The planes formed by the CoS$_3$N metallocycle and by N(1), Co, N(2) are nearly perpendicular to each other (88.3°). One of the nitrosyl oxygen atoms (O(1)) lies within, and the other one 72(5) pm below the N(1), Co, N(2) plane. Due to the small 'bite angle' of the chelate ligand, the S(1)–Co–S(3) angle is only 91.80(6)° and the coordination tetrahedron at the cobalt atom is slightly distorted. In the dithioacetylacetonate complex, Co(NO)$_2$(SacSac), where the cobalt has a similar environment, this angle is opened to 100.0(1)° [16]. The Co–S bond lengths in this latter complex are somewhat shorter (mean 222.0 pm) than in *5*.

Experimental

The reactions were carried out under N$_2$ in pentane which had been dried over CaH$_2$ and saturated with N$_2$. S$_4$N$_4$ was prepared according to the literature [15]; it contained appreciable amounts of S$_8$.

To a solution of Co$_2$(CO)$_8$ (0.88 g, 2.57 mmol) in 60 ml pentane was added S$_4$N$_4$ (0.95 g, 5.15 mmol), and the mixture was stirred for 2 hrs. Evolution of CO occurred, and a black product precipitated which was washed several times with pentane. A suspension of this black intermediate in pentane was stirred for 24 hrs under an atmosphere of NO. The violet solution was filtered and the solvent evaporated in an aspirator vacuum. The product was sublimed from the residue under high vacuum to give 0.14 g violet Co(NO)$_2$(S$_3$N) (0.61 mmol, 12%) which slowly decomposed at ambient temperature.

If the violet solution containing *5* was brought to dryness, the resulting residue could not be completely redissolved in pentane. Similar observations have been made with Co(NO)$_2$(SacSac) (SacSac = dithioacetylacetonate) [13].

Crystals suitable for an X-ray crystallographic study were obtained by cooling a concentrated pentane solution to −25 °C.

Crystal Data and Structure Determination of $Co(NO)_2(S_3N)$ (5)

Crystals of *5* are monoclinic with $a = 616.4(3)$, $b = 1532(1)$, $c = 734.9(3)$, $\beta = 103.47(4)$, $V = 675 \cdot 10^6$ pm^3. Space group $P2_1/c$ ($Z = 4$), determined by precession photographs*, σ (calc.) = 2.25 g/cm^3. Intensity data were collected on a Syntex $P2_1$ four circle automatic diffractometer using Mo-K$_\alpha$ radiation (graphite monochromator, $\lambda = 71.069$ pm, ω-scan, $\Delta\omega = 0.9°$, 1053 independent reflections, $2° \leqslant 2\theta \leqslant 48°$). The data were corrected for Lorentz and polarizations factors, but not for absorption (μ(Mo-K$_\alpha$) = 34.5 cm^{-1}). The structure was solved by the heavy atom method and refined by full matrix least squares, treating all atoms with anisotropic thermal parameters. For 868 structure factors with $F_o \geqslant 4.0\ \sigma(F_o)$, final $R_1 = 0.038$ and $R_2 = 0.037$ were obtained. The final atomic coordinates and thermal parameters are given in Table V.

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