

2.5 mdynes/Å., but variable since the Hg–Hg distance is a function of the anions in the compound), and also with that for the I<sub>2</sub> molecule (1.7 mdynes/Å.), which has a bond energy of 36 kcal./mole.

### Experimental

The rhenium carbonyl was a gift of Alpha Inorganics. The powder sample was compressed into a wafer and the Raman spectrum was recorded using a Cary Model 81 Raman spectrophotometer. We are grateful to Professor R. C. Lord and Dr. Claron Hoskins for their assistance with these measurements. Due to the small quantity of material available and the difficulties inherent in the measurement of Raman spectra of solid materials, accurate measurements of the polarizations of the bands were not possible. For all bands the polarization ratios were found to be  $0.65 \pm 0.15$ . These results are not inconsistent

with the assignments made, but they do not provide any definite support for them either.

The overtone and combination spectra were recorded on a Cary Model 14 spectrograph, using solutions in fresh Fisher Certified reagent carbon tetrachloride in quartz cells of path length 5 cm. Monitoring of the Mn<sub>2</sub>(CO)<sub>10</sub> solution with infrared in the 2200–1900 cm.<sup>-1</sup> region immediately indicated slight reaction to form ClMn(CO)<sub>5</sub> (*i.e.*, the strongest  $\nu_4$  (E) band of ClMn(CO)<sub>5</sub> was barely perceptible). The ClMn(CO)<sub>5</sub> combination band  $\nu_2 + \nu_4$  appeared at 4200 cm.<sup>-1</sup> in the near-infrared spectrum at fairly low intensity, about 10% of the strongest ( $\nu_1 + \nu_5$ ) band of Mn<sub>2</sub>(CO)<sub>10</sub> (see Figure 4). A near-infrared spectrum of ClMn(CO)<sub>5</sub> was run and indicated that the band at 4200 cm.<sup>-1</sup> is stronger by a factor of about 2 than the two next strongest bands. When dilute solutions of Mn<sub>2</sub>(CO)<sub>10</sub> are prepared using previously opened, shelf aged CCl<sub>4</sub>, the major constituent is ClMn(CO)<sub>5</sub>.

CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA, AND  
THE WILLIAM RAMSEY AND RALPH FORSTER LABORATORIES,  
UNIVERSITY COLLEGE, LONDON, ENGLAND

## Metal Nitrosyls. VI. Some New Six-Coordinate Mononitrosyl Complexes of Cobalt<sup>1</sup>

By ROBERT D. FELTHAM<sup>2</sup> AND R. S. NYHOLM

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A new series of six-coordinated mononitrosyl complexes of cobalt has been prepared. These complexes, stabilized using the bidentate ligands ethylenediamine and *o*-phenylenebis(dimethylarsine), are of the type [CoXNOL<sub>2</sub>]<sup>+</sup>. The infrared and electronic spectra of these mononitrosyl complexes show them to be complexes of cobalt(III). One five-coordinate cobalt compound has also been prepared and is discussed.

### Introduction

Numerous cobalt nitrosyls have been prepared before,<sup>3</sup> but there are only two nitrosyl compounds in which cobalt is known to be six-coordinated. These two compounds contain the [Co(CN)<sub>5</sub>NO]<sup>3-</sup> and the black [CoNO(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ions.<sup>4,5</sup> In order to interpret the spectroscopic behavior of metal nitrosyls more easily, it was desirable to prepare a series of six-coordinated complexes which were relatively stable, which contained only a single nitrosyl group as one of the six ligands, and which could be readily compared with compounds of a similar geometry.

The ligands ethylenediamine (en) and *o*-phenylenebis(dimethylarsine) (das), first prepared by Chatt and Mann,<sup>6</sup> were selected as the stabilizing ligands since so many compounds of cobalt containing these ligands

are known. The compounds [CoX<sub>2</sub>(das)<sub>2</sub>] can be isolated as stable crystalline solids.<sup>7</sup> Therefore, these compounds were selected initially for reaction with NO.

### Experimental

**Materials and Analyses.**—All of the reactions were carried out under nitrogen which was passed over pellets of "BTS" catalyst obtained from Badische-Anilin and Soda Fabrik, Ludwigshafen, Germany. This treatment is supposed to reduce the oxygen level in the nitrogen to 0.1 p.p.m. The compounds [CoX<sub>2</sub>(das)<sub>2</sub>] were prepared as has been previously described.<sup>7</sup> The en complexes of cobalt(II) were prepared *in situ* and allowed to react with NO without isolation. The nitric oxide supplied by Matheson was purified by passing it through a trap at -78° and leading the effluent directly into the reaction vessel. No precautions were taken to remove water from the solvents, since it appeared that the reactions were not influenced by the presence or absence of water in the reaction media. The cobalt salts were obtained from City Chemical Corp. and Fisher Scientific Co.

The elemental analyses were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colo.; Messrs. Weiler and Strauss, Oxford; Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.; and the University College Analytical Laboratory.

**Reactions of NO with [CoX<sub>2</sub>(das)<sub>2</sub>].**—A sample of the cobalt(II) complex [CoX<sub>2</sub>(das)<sub>2</sub>] was suspended or dissolved in the appropriate solvent, the system was purged with oxygen-free nitrogen, and NO<sub>2</sub>-free NO was bubbled through the solution. When the reaction was complete, as indicated by the color or solubility of the materials, the undissolved solids were removed from the solu-

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964. For the previous paper in this series, see R. D. Feltham and W. G. Fateley, *Spectrochim. Acta*, **20**, 1081 (1964).

(2) Department of Chemistry, University of Arizona, Tucson, Ariz. North Atlantic Treaty Organization Postdoctoral Fellow.

(3) For example, see (a) A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, **199**, 483 (1963); (b) W. Hieber and K. Heinicke, *Z. anorg. allgem. Chem.*, **316**, 305 (1962); (c) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(4) (a) R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964); (b) E. P. Bertin, S. Mizushima, T. J. Lance, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 382 (1959).

(5) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958).

(6) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 610 (1939).

(7) R. S. Nyholm, *ibid.*, 2071 (1950).

tion by filtration and the filtrate was cooled below room temperature to crystallize the products. Several preliminary experiments of this type were carried out in order to find the best solvent for these reactions. It was found that acetone gave only a nitro (nitrito) complex, nitrobenzene gave an impure nitrosyl, and methanol gave a relatively pure nitrosyl complex.

Using methanol as the solvent, NO was bubbled through a slurry of 1 g. of the insoluble yellow complex  $[\text{CoBr}_2(\text{das})_2]$ . After 1.5 hr. the red solution was filtered, and the filtrate was cooled to  $0^\circ$ . This treatment yielded well-formed red crystals which were separated by filtration and dried by washing with a small amount of diethyl ether. Duplicate samples and the results from different analysts indicate that the arsenic analyses are less reliable than those of the other elements.

$[\text{CoBrNO}(\text{C}_6\text{H}_4[\text{As}(\text{CH}_3)_2]_2)_2][\text{Br}]$  (color, red-brown). *Anal.* Calcd.: C, 29.26; H, 3.93; As, 36.51; N, 1.71; O, 1.95; Br, 19.47. Found: C, 29.22; H, 4.22; As, 34.64; N, 1.58; O, 0.91; Br, 19.73;  $\chi_g = -0.322 \times 10^{-6}$  c.g.s. unit.

The following compounds were prepared in an analogous way except that the cobalt *o*-phenylenebis(dimethylarsine) chloride, iodide, or perchlorate was used instead of the bromide.

$[\text{CoClNO}(\text{C}_6\text{H}_4[\text{As}(\text{CH}_3)_2]_2)_2][\text{Cl}]$  (color, red-brown). *Anal.* Calcd.: C, 32.81; H, 4.41; As, 40.94; N, 1.91; O, 2.19; Cl, 9.69. Found: C, 32.75; H, 4.55; As, 40.17; N, 1.73; O, 2.37; Cl, 10.69.

$[\text{CoINO}(\text{C}_6\text{H}_4[\text{As}(\text{CH}_3)_2]_2)_2][\text{I}]$  (color, brown). *Anal.* Calcd.: C, 26.25; H, 3.53; As, 32.76; N, 1.53; O, 2.19; I, 27.71. Found: C, 26.71; H, 3.89; As, 31.90; N, 1.81; O, 2.10; I, 27.65.

$[\text{CoNO}(\text{C}_6\text{H}_4[\text{As}(\text{CH}_3)_2]_2)_2][\text{ClO}_4]_2$  (color, red). *Anal.* Calcd.: C, 27.93; H, 3.75; As, 34.85; N, 1.63; O, 16.74; Cl, 8.25. Found: C, 28.03; H, 3.91; As, 35.57; N, 1.82; O, 16.39; Cl, 7.43.

The thiocyanate complex was obtained by first preparing  $[\text{CoCl}_2(\text{das})_2]$ , adding sodium thiocyanate, and bubbling NO through the solution as described above.

$[\text{Co}(\text{NCS})\text{NO}(\text{C}_6\text{H}_4[\text{As}(\text{CH}_3)_2]_2)_2][\text{NCS}]$  (color, brown). *Anal.* Calcd.: C, 33.99; H, 4.15; As, 38.56; N, 5.41; O, 2.06; S, 8.25. Found: C, 33.99; H, 4.27; As, 38.80; N, 5.22; O, 2.67; S, 8.58.

**Reactions of NO with  $[\text{CoX}_2(\text{en})_2]$ .**—Since it was not possible to isolate the intermediate cobalt(II)-en complex, all reactions were carried out without purifying the intermediates.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (9.5 g.) was dissolved in 150 ml. of methanol, 2 moles of ethylenediamine per mole of cobalt (5.0 ml.) was added to the solution, the solution was purged with oxygen-free nitrogen, and NO was bubbled through the solution until there was no further uptake of NO (about 1 hr.). The solution was freed of NO by purging with  $\text{N}_2$  and was filtered to remove the solids which had formed. The blood-red filtrate was cooled to  $-78^\circ$ . The brown crystalline solid which formed was impure and was recrystallized from methanol under nitrogen to give a material which was analytically pure.

$[\text{CoClNO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{Cl}]$  (color, brown). *Anal.* Calcd.: C, 17.15; H, 5.76; N, 25.01; O, 5.71; Cl, 25.32; Co, 21.05. Found: C, 17.01; H, 6.26; N, 25.35; O, 5.64; Cl, 25.21; Co, 19.74;  $\chi_g = -0.146 \times 10^{-6}$  c.g.s. unit.

The perchlorate proved to be more easily isolable, and consequently the other halides were prepared from the diperchlorate. Cobalt(II) perchlorate hexahydrate was dissolved in methanol, en was added to the solution (Co:en = 1:2), the solution was purged with oxygen-free nitrogen, and NO was bubbled through the solution until the uptake of NO had ceased. The red crystalline precipitate which had formed was separated by filtration, washed with a small amount of ether, and dried in a desiccator containing molecular sieves.

$[\text{CoNO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{ClO}_4]_2$  (color, red). *Anal.* Calcd.: C, 11.77; H, 3.95; N, 17.16; O, 35.29; Cl, 17.38. Found: C, 12.53; H, 4.31; N, 17.54; O, 37.30; Cl, 17.15;  $\chi_g = +0.088 \times 10^{-6}$  c.g.s. unit.

The following compounds were prepared by dissolving the nitrosyl perchlorate in acetone, adding the lithium salt slowly,

and separating the insoluble perchlorate by filtration. The product was washed with a large volume of acetone, in which it was insoluble, then with ether, and finally air dried.

$[\text{CoClNO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{ClO}_4]$  (color, brown). *Anal.* Calcd.: C, 13.96; H, 4.69; N, 20.36; O, 23.25; Cl, 20.61. Found: C, 13.95; H, 4.39; N, 19.90; O, 22.81; Cl, 20.40.

$[\text{CoBrNO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{ClO}_4]$  (color, brown). *Anal.* Calcd.: C, 12.36; H, 4.15; N, 18.03; O, 20.57; Br, 20.57; Cl, 9.13. Found: C, 13.05; H, 4.52; N, 17.89; O, 23.02; Br, 23.40; Cl, 7.79.

$[\text{CoINO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{ClO}_4]$  (color, dark brown). *Anal.* Calcd.: C, 11.03; H, 3.70; N, 16.08; O, 18.37; I, 29.14; Cl, 8.14. Found: C, 11.12; H, 3.82; N, 16.48; O, 15.85; I, 28.70; Cl, 8.14.

$[\text{Co}(\text{NO}_2)\text{NO}(\text{C}_2\text{H}_4[\text{NH}_2]_2)_2][\text{ClO}_4]$  (color, red-brown). *Anal.* Calcd.: C, 12.96; H, 4.55; N, 22.68; O, 34.45; Cl, 9.57. Found: C, 13.06; H, 4.18; N, 22.78; O, 34.66; Cl, 9.60.

All of these nitrosyl complexes are more or less sensitive to air oxidation while in solution. All operations which required the use of solutions of these complexes were therefore carried out under nitrogen. It was found that these compounds were sufficiently stable to air that they could be ground or milled with Nujol or halocarbons in air with no deleterious effects. Some of the properties of these complexes are summarized in Table I.

TABLE I  
A SUMMARY OF SOME PROPERTIES OF THE  
COBALT NITROSYL COMPLEXES

Compound	NO freq., cm. <sup>-1</sup>	$\Delta g$ in nitro- methane	Slope ( $\Delta g - A_g$ )/ $\sqrt{c}$	Elec- tro- lyte type
$[\text{CoBrNO}(\text{das})_2]\text{Br}$	1565, 1550	93.8	150	1:1
$[\text{CoClNO}(\text{das})_2]\text{Cl}$	1562, 1548	Dec.	Dec.	...
$[\text{CoINO}(\text{das})_2]\text{I}$	1576, 1555	96.5	213	1:1
$[\text{CoNO}(\text{das})_2][\text{ClO}_4]_2$	1852	126.5	571	2:1
$[\text{Co}(\text{NCS})\text{NO}(\text{das})_2]\text{NCS}$	1587, 1561	...	...	...
$[\text{CoClNO}(\text{en})_2]\text{Cl}$	1635	(125) <sup>a</sup>	(750)	2:1
$[\text{CoNO}(\text{en})_2][\text{ClO}_4]_2$	1663	105.8	1015	?
		(176) <sup>b</sup>	(1400)	?
$[\text{CoClNO}(\text{en})_2]\text{ClO}_4$	1611	101.3	172	1:1
$[\text{CoBrNO}(\text{en})_2]\text{ClO}_4$	1640	...	...	...
$[\text{CoINO}(\text{en})_2]\text{ClO}_4$	1654	...	...	...
$[\text{Co}(\text{NO}_2)\text{NO}(\text{en})_2]\text{ClO}_4$	1643	...	...	...

<sup>a</sup> In methanol. <sup>b</sup> In water. <sup>c</sup> Mhos equiv.<sup>-1</sup>.

**Physical Measurements.**—The infrared spectra were run as Nujol and halocarbon mulls on a Beckman IR-9 spectrophotometer or on a Perkin-Elmer Infracord. The reflectance spectra were measured using a Zeiss PMQ II spectrophotometer with a reflectance attachment RA 2 and a specially constructed PbS detector for measurements between 4000 and 16,500 cm.<sup>-1</sup> which was obtained from Carl Zeiss, Oberhochen, Germany. The reference was prepared from LiF (optical) obtained from K and K Laboratories, Jamaica, N. Y. The conductivity measurements were carried out under nitrogen using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. The concentration ranged from  $5 \times 10^{-5}$  to  $10^{-3}$  M.

## Results

**Infrared Spectra.**—With the exception of  $[\text{CoNO}(\text{das})_2][\text{ClO}_4]_2$ , all of the compounds which were prepared had strong absorption bands in the infrared region between 1550 and 1650 cm.<sup>-1</sup>. This frequency region is normally associated with compounds containing double bonds in groups such as  $\text{N}=\text{O}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{N}=\text{N}$ , etc.<sup>8</sup> The infrared spectra of the cobalt

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1964.

nitrosyls described below are consistent with there being a double bond between the nitrogen and oxygen.

It was especially easy to distinguish the NO frequencies in the case of the das complexes, since the 1600  $\text{cm}^{-1}$  region is free from ligand absorptions. The NO frequencies in the en compounds were a little more difficult to identify, because en itself has moderately strong absorption bands in the 1600  $\text{cm}^{-1}$  region.<sup>9</sup> However, by direct comparison with similar types of compounds, the positions of the NO stretching frequencies could be identified. The infrared spectra of several cobalt compounds of the type *cis*- and *trans*-[CoAB(en)<sub>2</sub>][X] have been examined.<sup>10</sup> Baldwin concluded from this study that the *cis* compounds are distinguished by the presence of two distinct, well-separated bands between 870 and 900  $\text{cm}^{-1}$ , while the *trans* members of this series have only one band (sometimes with a slight shoulder) in this same region. Since these results were independent of the groups A, B, and X, but only dependent on groups A and B being *cis* or *trans* to one another, this region of the infrared spectrum was used to indicate the configuration of the nitrosyl compounds. With the exception of the iodide, the nitrosyl compounds had only a single absorption band at 890  $\text{cm}^{-1}$ , and therefore on this basis this series of cobalt ethylenediamine nitrosyl complexes is assigned to the *trans* configuration.

The complex [Co(NO<sub>3</sub>)NO(en)<sub>2</sub>][ClO<sub>4</sub>], which was prepared by treating the diperchlorate with lithium nitrate, has nitrate frequencies at 1395, 1322, and 824  $\text{cm}^{-1}$  which are typical for coordinated nitrate groups.<sup>11</sup> The other frequency for the coordinated nitrate group usually found in the 1000  $\text{cm}^{-1}$  region could not be distinguished from the strong absorption of the perchlorate group.

The infrared spectrum of [Co(ClO<sub>4</sub>)NO(en)<sub>2</sub>][ClO<sub>4</sub>] is more difficult to interpret. Since en itself absorbs in the 1100  $\text{cm}^{-1}$  region, it is impossible to determine whether or not the perchlorate band at 1100  $\text{cm}^{-1}$  is split. However, from the fact that the NO frequency in this perchlorate complex is so similar in all respects to the other members of this series and the reflectance spectra throughout the near-infrared, visible, and near-ultraviolet regions are also very similar (*vide infra*), it was concluded that this complex is a six-coordinate species.

The results which were obtained from the das complexes are quite similar to those described above for the en complexes. The NO frequencies of the das complexes are approximately 100  $\text{cm}^{-1}$  lower than those of the corresponding en complexes. There are also two NO frequencies present in all of the das complexes except the perchlorate. Several attempts were made to separate the compounds which give rise to these two NO frequencies. When [CoBrNO(das)<sub>2</sub>][Br] was recrystallized, the relative intensities of the two NO

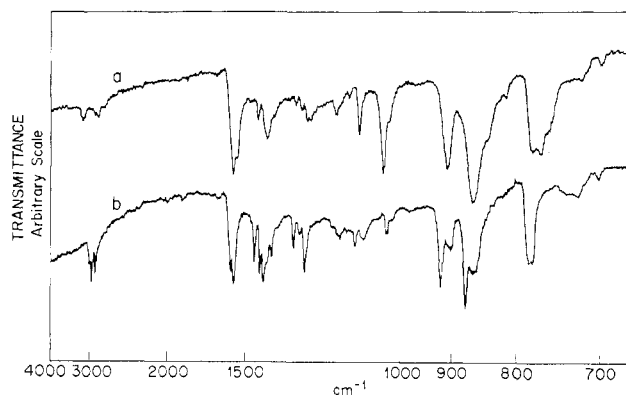


Figure 1.—The infrared spectra of [CoBrNO(das)<sub>2</sub>][Br]: a, mostly *cis*; b, mostly *trans*.

bands differed by as much as 100% from the relative intensities of these NO bands in the material as originally obtained from methanol. The elemental analyses indicate that these materials have the same composition, but neither isomer could be obtained completely free from contamination by the other isomer. There are also important differences in the 900  $\text{cm}^{-1}$  region of the infrared spectra of these materials (Figure 1). The absorption bands at approximately 920 and 860  $\text{cm}^{-1}$  have been assigned by Rodley<sup>12</sup> to the (CH<sub>3</sub>)<sub>2</sub>As deformations. Rodley studied several *cis* and *trans* isomers of the type [CoX<sub>2</sub>(das)<sub>2</sub>]<sup>+</sup> and found that in the case of the *cis* isomers these bands at 920 and 860  $\text{cm}^{-1}$  are each single bands, or have only slight shoulders, while in the case of the *trans* isomers these bands are both split into doublets. The pattern of the two bands at 920 and 860  $\text{cm}^{-1}$ , which was obtained for [CoBrNO(das)<sub>2</sub>][Br] that had been recrystallized from methanol, corresponds exactly to the pattern which was found for the *trans* isomers studied by Rodley. Similarly, in the case of the [CoBrNO(das)<sub>2</sub>][Br] which had not been recrystallized, the bands at 920 and 860  $\text{cm}^{-1}$  were each single, corresponding to the spectra of the *cis* isomers studied by Rodley. The X-ray powder patterns of these compounds were also compared. The powder patterns of the nitrosyl compound, whose infrared spectrum corresponds to that of the *trans* dihalide complexes, were almost identical and were completely unlike the X-ray powder patterns of the *cis* complexes. Therefore, the isomer with the lower NO frequency and doublets at 920 and 860  $\text{cm}^{-1}$  was assigned to the *trans* configuration while the isomer with the higher NO frequency and single absorption bands at 920 and 860  $\text{cm}^{-1}$  was assigned to the *cis* configuration.

Except for the NO region at 1550  $\text{cm}^{-1}$  there are only slight differences between the infrared spectra of *trans*-[CoCl<sub>2</sub>(das)<sub>2</sub>][Cl] and [CoClNO(das)<sub>2</sub>][Cl]. Although the higher NO frequency of the *cis* complex at 1562  $\text{cm}^{-1}$  is a quite prominent feature of the spectrum, there appears to be only a small amount of this *cis* complex present.

In contrast to this, the infrared spectrum of [CoNO(das)<sub>2</sub>][I] suggests that this complex consists al-

(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 186-189.

(10) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

(11) C. C. Addison and B. M. Gatehouse, *ibid.*, 613 (1960).

(12) G. A. Rodley, Thesis, University of London, April 1963.

most entirely of the *cis* isomer. There are only single absorption bands at 865 and 910  $\text{cm}^{-1}$ , and there is only a slight shoulder at 1555  $\text{cm}^{-1}$  on the low-frequency side of the NO band.

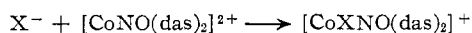
The thiocyanate complex clearly has two different thiocyanate groups present in the molecule, since there are two CN stretching frequencies which are well separated at 2079 and 2060  $\text{cm}^{-1}$ . From the position of the two C-S frequencies at 850  $\text{cm}^{-1}$  coordinated and 729  $\text{cm}^{-1}$  uncoordinated, it was concluded that the nitrogen of the thiocyanate group is coordinated to cobalt in a manner similar to compounds of other transition elements of the first row<sup>13</sup> (Table II). The higher NO frequency is very much more intense than the lower NO frequency. From this relative intensity of the two NO frequencies, and from the lack of splitting of the two frequencies at 871 and 913  $\text{cm}^{-1}$ , it was concluded that the thiocyanate complex consists mainly of the *cis* form.

TABLE II  
SOME INFRARED FREQUENCIES ( $\text{CM}^{-1}$ ) OF THE  
COBALT NITROSYL THIOCYANATE COMPLEXES

	Vibration		
	C-N	C-S	C-N-S bend
KCNS	2053	749	484
NCS complexes <sup>13</sup>	2120-2065	760-880	466-479
SCN complexes <sup>13</sup>	2132-2046 (or 2066)	694-723	415-479
[Co(NCS)NO(das) <sub>2</sub> ]- [NCS]	2079, <sup>a</sup> 2060 <sup>b</sup>	850, <sup>a</sup> 729 <sup>b</sup>	464, <sup>a</sup> ...

<sup>a</sup> Coordinated. <sup>b</sup> Uncoordinated.

Among all of the compounds of this series, the compound [CoNO(das)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> is unique. The first and most obvious fact of all is that the NO frequency in this complex occurs at 1852  $\text{cm}^{-1}$ . This is approximately 300  $\text{cm}^{-1}$  higher than for any of the other members of this series of nitrosyls. Chemically, these species are closely related, since the halogen complexes may be prepared by allowing the perchlorate to react with chloride, bromide, or iodide ions in methanol. This reaction is fast, and appears to be the simple addition reaction



In comparison with the en perchlorate complex, the perchlorate band at 1090  $\text{cm}^{-1}$  in this das compound is single and very sharp. A shoulder at 1105  $\text{cm}^{-1}$  is present as a medium to strong band in all of the das complexes and therefore is not a perchlorate vibration. Although these data (infrared, powder patterns, chemical reactions) suggest that in the crystalline state the cobalt atom is five-coordinate, an X-ray study is needed to establish the number of atoms in the coordination sphere conclusively.

**Conductivity.**—The conductances of several of these complexes were determined using the method described previously.<sup>14</sup> The results of these measurements sum-

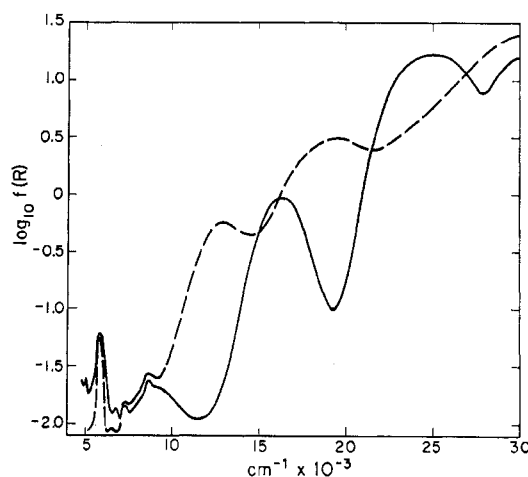


Figure 2.—The reflectance spectra of *trans*-[CoCl<sub>2</sub>(das)<sub>2</sub>][Cl] (—) and [CoClNO(das)<sub>2</sub>][Cl] (---).

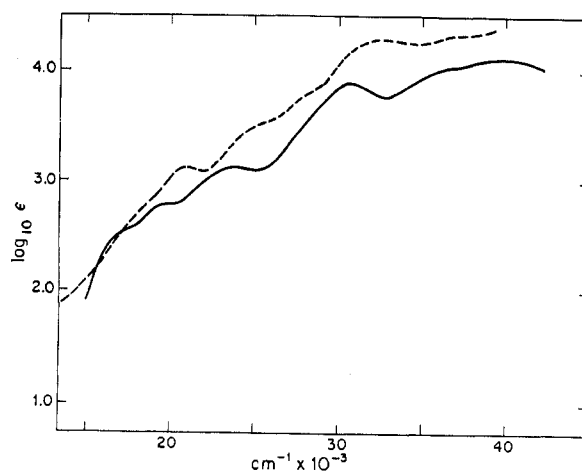


Figure 3.—The visible and ultraviolet spectra of (a) *cis*-[CoBr<sub>2</sub>(das)<sub>2</sub>][ClO<sub>4</sub>] (—) in ethanol; (b) *cis*-[CoINO(das)<sub>2</sub>][I] (---) in dimethyl sulfoxide.

marized in Table I show that all of the complexes of the type [CoXNO(das)<sub>2</sub>]<sup>+</sup>X where X excludes ClO<sub>4</sub><sup>-</sup> are univalent-univalent electrolytes in nitromethane, thus establishing these complexes as being six-coordinate with the halide ion occupying the sixth coordination position. The compound [CoNO(das)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> is a univalent-divalent electrolyte in nitromethane, which confirms the conclusion drawn from the infrared and visible spectra that this compound is five-coordinate (at least in the solid state) and that the perchlorate anion is not coordinated to the cobalt. The results of conductivity measurements on [CoNO(en)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> in both nitromethane and water indicate that this complex is polymeric and therefore six-coordinate, but the way in which the complex is polymerized cannot be resolved without further information.

**Reflectance Spectra.**—The reflectance spectra of all of these complexes have been measured and have been compared with the spectra of other cobalt complexes of the type: *cis*- and *trans*-[CoX<sub>2</sub>(das)<sub>2</sub>]<sup>+</sup> and [CoX<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>. The spectra of [CoClNO(das)<sub>2</sub>][Cl], which was assigned to the *trans* configuration on the basis of its infrared spectrum, and *trans*-[CoCl<sub>2</sub>(das)<sub>2</sub>][Cl],

(13) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(14) R. D. Feltham and R. G. Hayter, *ibid.*, 4587 (1964).

TABLE III  
 ELECTRONIC ABSORPTION SPECTRA OF THE COBALT NITROSYL COMPLEXES<sup>a</sup>

Compound	Band A		Band B		Band I		Band II	
	( $\epsilon$ )	( $\epsilon$ ) <sup>c</sup>	( $\epsilon$ )	( $\epsilon$ ) <sup>c</sup>	Ia ( $\epsilon$ )	Ib ( $\epsilon$ )	( $\epsilon$ )	( $\epsilon$ ) <sup>c</sup>
<i>trans</i> -[CoBrNH <sub>3</sub> (en) <sub>2</sub> ] <sup>2+</sup>	11.1	(4.7)	12.9	(...)	18.4 (51)	22.1 (20)	27.8	(46)
<i>trans</i> -[CoINH <sub>3</sub> (en) <sub>2</sub> ] <sup>2+</sup>	10.9	(30)	13.7	(...)	17.4 (71)	Unobsd.		
<i>trans</i> -[CoNO(CH <sub>3</sub> OH)(en) <sub>2</sub> ] <sup>2+</sup>	10.8	(~4.0)	13.5	(32)	18.0 (83)	22.2 (138)	28.2	(~360)
<i>trans</i> -[CoClNO(en) <sub>2</sub> ][Cl] <sup>b</sup>	9.0	(...)	13.5	(...)	18.0 (...)	22.7 (...)	28.0	(...)

<sup>a</sup> The units are  $\text{cm}^{-1} \times 10^{-3}$ . <sup>b</sup> Observed as reflectance spectrum only. <sup>c</sup> The units are  $\text{l. mole}^{-1} \text{cm}^{-1}$ .

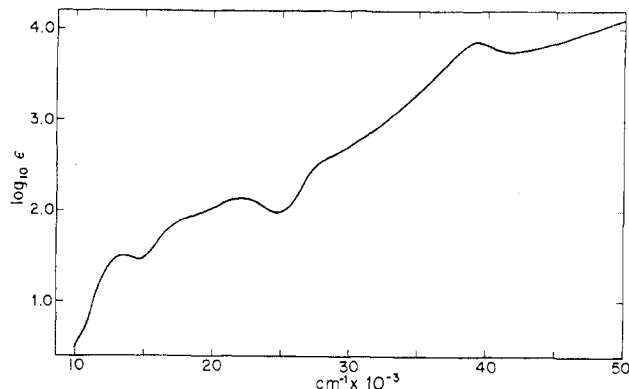


Figure 4.—The visible and ultraviolet spectrum of [CoClNO(en)<sub>2</sub>][Cl] in methanol.

the geometry of which has been established independently,<sup>15</sup> are compared in Figure 2. The number and positions of the absorption bands in these two compounds are very similar. There is a spin-forbidden band in each of these compounds at approximately 10,000  $\text{cm}^{-1}$ . The first spin-allowed band occurs approximately 2000  $\text{cm}^{-1}$  higher in energy in the nitrosyl than in the chloride, while the second and third spin-allowed bands come almost at the same position in both compounds. The solution spectra of *cis*-[CoBr<sub>2</sub>(das)<sub>2</sub>]<sup>+</sup> (data taken from ref. 15) and *cis*-[CoINO(das)<sub>2</sub>]<sup>+</sup> are compared in Figure 3. The spectra are quite distinct from those of the *trans* compounds in Figure 2, but are very similar to each other. The spectrum of the nitrosyl iodide corresponds closely to the spectra of the other known *cis* compounds, but the spectrum of the *trans* nitrosyl chloride is somewhat different from that of the other known *trans* compounds. There are two possible explanations for this. First of all, it has thus far proved impossible to obtain pure samples of the *trans* compounds which are free from the *cis* isomer. It may be that these small amounts of the *cis* isomer are contributing significantly to the spectra which have been presented here. It must also be noted that in *trans*-[CoX<sub>2</sub>(das)<sub>2</sub>]<sup>+</sup> ( $D_{4h}$ ) complexes there is a center of symmetry which is not present in *trans*-[CoXNO(das)<sub>2</sub>]<sup>+</sup> ( $C_{2v}$ ). If the X and NO ligands give rise to similar ligand fields, there may be a pseudo-center of symmetry, and the spectra of the two *trans*-complexes could be nearly identical. If X and NO have different effective ligand fields, as might be expected, then the spectra of the *trans* isomers will not be identical. The spectrum of *cis*-[CoBrNO(das)<sub>2</sub>]-

[ClO<sub>4</sub>] was measured in methanol. It has essentially the same spectrum as do the thiocyanate and iodide, except that the charge-transfer spectrum is further into the ultraviolet region of the spectrum. Again, the spectrum observed for the *cis* bromide complex is essentially the same as that observed for *cis*-[CoBr<sub>2</sub>(das)<sub>2</sub>][Br] and it is obviously different from the spectrum of *trans*-[CoBrNO(das)<sub>2</sub>][Br].

To ascertain if the first band which is observed in these complexes between 12,000 and 13,000  $\text{cm}^{-1}$  is a spin-allowed or a spin-forbidden transition, the spectrum of [CoClNO(en)<sub>2</sub>][Cl] was measured in solution (Figure 4). Although the conductance experiments indicate that the complex which is present in solution is the methanolo complex, the positions of the bands in the chloride and methanolo complex are similar enough that the absorption band at 13,000  $\text{cm}^{-1}$  in the methanol complex can be used to estimate the intensity of the band at 13,000  $\text{cm}^{-1}$  in the chloro complex. The intensity of the band at 13,000  $\text{cm}^{-1}$  corresponds well to those<sup>16</sup> observed for [CoXNH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup>, which had values of  $\epsilon$  as high as 30. The positions and intensities of the absorption bands of [CoNO(CH<sub>3</sub>OH)(en)<sub>2</sub>]<sup>2+</sup>, [CoBrNH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup>, and [CoINH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup> (Table III) indicate that a close relationship exists between the electronic states of these compounds. Thus the electronic spectrum of [CoNO(CH<sub>3</sub>OH)(en)<sub>2</sub>]<sup>2+</sup> can be interpreted in terms of a Co(III) ion surrounded by an array of ligands with an effective ligand field similar to the ligand field in the complex [CoBrNH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup>. Both [CoBrNH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup> and [CoNO(CH<sub>3</sub>OH)(en)<sub>2</sub>]<sup>2+</sup> have two spin-forbidden bands at approximately the same energy (10,000 and 13,000  $\text{cm}^{-1}$ ), two spin-allowed bands from the <sup>1</sup>T<sub>1</sub> level (18,000 and 23,000  $\text{cm}^{-1}$ ), and a spin-allowed band from the <sup>1</sup>T<sub>2</sub> level in the octahedral approximation of the ligand field bands. This interpretation requires the NO ligand to be formulated as (N=O)<sup>-</sup> and places the (N=O)<sup>-</sup> ligand in these cobalt complexes somewhere between bromide and iodide in the spectrochemical series. This formulation for the NO ligand in these cobalt complexes is confirmed by the NO stretching frequencies of these compounds (*vide supra*).

Another salient feature is that the charge-transfer bands are in the same positions (40,000 and 33,000  $\text{cm}^{-1}$ ) with the same relative molar extinction coefficients as was observed for [CoBrNH<sub>3</sub>(en)<sub>2</sub>]<sup>2+</sup>. The position and number of the charge-transfer bands in [CoNO(CH<sub>3</sub>OH)(en)<sub>2</sub>]<sup>2+</sup> indicates that the charge-

(15) T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962).

(16) T. Yasui and Y. Shimura, *Bull. Chem. Soc. Japan*, **36**, 1286 (1963).

transfer spectrum is from  $(\text{N}=\text{O})^-$  to cobalt, just as are the charge-transfer bands in the halogen complexes of cobalt(III).<sup>17</sup>

The pentacoordinate complex,  $[\text{CoNO}(\text{das})_2][\text{ClO}_4]_2$ , again deserves special consideration. The reflectance spectrum of the complex is quite different from that of the other nitrosyl complexes of this series, having no absorption bands below  $19,000 \text{ cm}^{-1}$ . There are two bands at  $25,000 \text{ cm}^{-1}$ , which are probably due to d-d transitions. Although it is not yet clear what the formal oxidation state of cobalt is in this five-coordinate nitrosyl, it probably consists of NO coordinated to Co(II) with spin pairing between the odd electron on the NO ligand and the Co(II), thus accounting for the observed diamagnetism of the compound. Further study is needed before drawing any final conclusions about the bonding in this five-coordinate complex.

### Summary

With the exception of  $[\text{CoNO}(\text{das})_2][\text{ClO}_4]_2$ , the properties of the mononitrosyl compounds of cobalt reported above can be described in terms of a model which consists of a Co(III) ion coordinated to  $(\text{N}=\text{O})^-$  and five other ligands. This model is capable of correlating such diverse observations as: (1) the observed NO stretching frequencies (typical of double bonds); (2) the presence of *cis* and *trans* isomers typical of Co(III); and (3) the ligand field and charge-transfer spectra, which are typical of those observed for other six-coordinate Co(III) compounds containing ligands other than NO. Further experiments are in progress to test the implications of such a model for other metal complexes containing NO groups with low NO stretching frequencies ( $1550 \text{ cm}^{-1}$ ).

(17) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

## Fluorophosphine Ligands. I. The Preparation and Characterization of Difluorophosphine

BY R. W. RUDOLPH AND R. W. PARRY

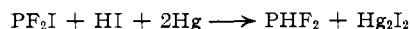
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From a reaction involving equal amounts of HI and  $\text{PF}_2\text{I}$  in the presence of free mercury, difluorophosphine has been isolated and characterized. The physical properties and spectral data for  $\text{PHF}_2$  are compared to those of  $\text{PH}_3$  and  $\text{PF}_3$ ; they indicate that  $\text{PHF}_2$  (a) is monomeric in the vapor, (b) is associated in the liquid, and (c) probably has a pyramidal structure. Basic hydrolysis of difluorophosphine yields hydrogen, indicative of its reducing properties.

### Introduction

Nitrogen has been known to form haloamines for some time.<sup>1-3</sup> The literature also mentions an attempted characterization of halophosphines, but no real halophosphines were ever isolated.<sup>4</sup> We wish to report the preparation and characterization of difluorophosphine,  $\text{PHF}_2$ .

Difluorophosphine was prepared by a reaction involving equal amounts of  $\text{PF}_2\text{I}^5$  and HI in the presence of free mercury. The equation is



A typical experiment resulted in a 55% yield of the fluorophosphine based on the amount of  $\text{PF}_2\text{I}$  taken.

### Experimental

**Apparatus.**—Standard high-vacuum techniques were used throughout.

(1) A. Kennedy and C. B. Colburn, *J. Am. Chem. Soc.*, **81**, 2906 (1959).

(2) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(3) R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929).

(4) P. Royen and K. Hill, *Z. anorg. allgem. Chem.*, **229**, 112 (1936).

(5) Phosphorus(III) iododifluoride was originally reported by R. G. Cavell, *J. Chem. Soc.*, **1992** (1964), to be unstable and disproportionate rapidly to  $\text{PF}_3$  and  $\text{PI}_3$ . Experiments in this laboratory indicate that  $\text{PF}_2\text{I}$  is reasonably stable. Complete characterization of this ligand and more of its chemistry will be presented in a future publication.

**Materials.**—Phosphorus(III) iododifluoride was prepared by the action of hydrogen iodide on dimethylamidophosphorous difluoride.<sup>6</sup> Hydrogen iodide was prepared by standard methods.<sup>7</sup>

**Preparation of Difluorophosphine.**—A 2.0-cc. sample of triply distilled mercury was placed in a 70-cc. reaction tube which was equipped with a stopcock and a standard taper joint. The tube was evacuated and 3.36 mmoles of  $\text{PF}_2\text{I}$  and 3.36 mmoles of HI were condensed into the tube at  $-196^\circ$ . After warming to  $25^\circ$  the tube was shaken for 1.5 hr. The tube was then opened to the Toepler system through two  $-196^\circ$  traps and 0.17 mmole of  $\text{H}_2$  (identified by gas density) was recovered. The products condensable at  $-196^\circ$  were passed through traps at  $-140$ ,  $-160$ , and  $-196^\circ$ . A 0.72-mmole sample of  $\text{PF}_3$  was trapped at  $-196^\circ$  and a 0.47-mmole sample of an unstable compound assumed to be  $\text{PHF}_2\text{HI}$  was retained at  $-140^\circ$ . This compound decomposed at room temperature to yield  $\text{PF}_3$ ,  $\text{SiF}_4$ , and yellow solids which contained iodine.<sup>8</sup>

A 1.85-mmole sample of the desired  $\text{PHF}_2$  was retained in the trap at  $-160^\circ$ . A second run using 1.52 mmoles of each reagent gave 0.84 mmole of  $\text{PHF}_2$ , 0.30 mmole of  $\text{PF}_3$ , 0.10 mmole of  $\text{H}_2$ ,

(6) This method for the preparation of pure phosphorus(III) monohalodifluorides was developed in this laboratory by (a) Sr. M. A. Fleming, Doctoral Dissertation, University of Michigan, 1963; (b) A. Moyé, unpublished results, University of Michigan, 1961, and reported independently by Cavell (ref. 5).

(7) C. J. Hoffman and E. A. Heintz, *Inorg. Syn.*, **7**, 180 (1963).

(8) In a separate experiment an equimolar mixture of  $\text{PF}_2\text{H}$  and HI decomposed to give  $\text{PF}_3$ ,  $\text{SiF}_4$ , and yellow solids which contained iodine.