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Four- and Five-Coordinated Nitrosyls of Cobalt Dithioacetylacetonate

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Two new cobalt nitrosyls $Co(NO)(C_5H_7S_2)_2$ and $Co(NO)_2(C_5H_7S_2)$ have been synthesized and characterized by spectroscopic and magnetic techniques. They are both monomeric nonelectrolytes and are considered to be simply constituted five- and four-coordinated complexes with pseudo-square-pyramidal and tetrahedral stereochemistries. The mononitrosyl $Co(NO)(C_5H_7S_2)_2$ disproportionates unexpectedly in solution to $Co(NO)_2(C_5H_7S_2)$ and $Co(C_5H_7S_2)_3$. The time dependence of this conversion has been followed by nmr and ir techniques.

Introduction

1,1- and 1,2-dithio chelates such as the dithiocarbamates and 1,2-dithiolenes are known to form a variety of mono- and dinitrosyls with the transition metals.[2,3] More recently it has been established that the 1,3-dithio chelate "dithioacetylacetone" (SacSac) is also compatible with nitric oxide and two complexes $Ru(NO)Cl(SacSac)_2$[4] and *cis*-$Fe(NO)_2(SacSac)_2$[5] have been characterized.

In the case of cobalt, dithiocarbamato complexes of the type $Co(NO)(S_2CNR_2)_2$ have been known[6] since 1931 although the rectangular-based pyramidal stereochemistry was not established until 30 years later.[7a] Related complexes with the formulation $[Co(NO)(dithiolene)_2]^{3-,2-,1-}$ have been synthesized.[8] A dinitrosyl of difluorodithiophosphate $Co(NO)_2(S_2PF_2)$ has also been synthesized[9] although there appears to be no instance in which both mono- and dinitrosyls have been obtained with the same dithio chelating ligand.[2,3]

It has been established that the square-planar cobalt(II) dithioacetylacetonate, $Co(SacSac)_2$, undergoes a variety of oxidative addition reactions with neutral and anionic chelating agents in the presence of molecular oxygen.[10,11] As an extension of these studies, the reaction between nitric oxide and $Co(SacSac)_2$ is of intrinsic interest and is reported here. In particular, it has been established that both a five-coordinated mononitrosyl $Co(NO)(SacSac)_2$ and a four-coordinated dinitrosyl $Co(NO)_2(SacSac)$ exist and their interconversion has been substantiated by infrared and nmr spectroscopy.

Experimental Section

Syntheses. $Co(NO)(C_5H_7S_2)_2$. Crystalline $Co(SacSac)_2$ (3.0 g) was suspended in CH_2Cl_2 (40 ml) at 0°. NO_2-free nitric oxide was passed through the deep violet slurry for 2 hr. The dark red solution obtained was filtered and an equal volume of petroleum ether (bp 30–40°) was added. The dark brown crystalline product which separated on cooling (0.8 g) was washed thoroughly with petroleum ether to remove any traces of $Co(NO)_2(SacSac)$.

$Co(NO)_2(C_5H_7S_2)$. Nitric oxide gas was passed into a CH_2Cl_2 solution (50 ml) of $Co(SacSac)_2$ (3.0 g) at room temperature (~20°) for 2 hr. The resulting red solution was taken to dryness under vacuum and the residue extracted with petroleum ether. The combined extracts were evaporated to dryness at room temperature and the solid dissolved in *n*-pentane. This solution was also quickly reduced to dryness and the dark red-brown crystals were collected and dried briefly at room temperature under vacuum (0.7 g).

Instrumentation and Materials. NO_2 was removed from cylinder nitric oxide by trapping it at −78°. Nmr spectra were obtained in $CDCl_3$ on JEOL and Varian 100-MHz instruments. Infrared spectra were measured in KBr disks or KBr solution cells on Perkin-Elmer 457 and 225 instruments. Other instrumental details have been described previously.[12]

Results and Discussion

For clarity the two new compounds are discussed separately in the first instance. Analytical and general data on the complexes are collected in Table I.

$Co(NO)(SacSac)_2$. The reaction at 0° of NO with a CH_2Cl_2 solution of the well-characterized square-planar $Co(SacSac)_2$ yields the dark brown crystalline complex of composition $Co(NO)(SacSac)_2$. This complex is nonconducting in nitromethane ($\lambda_M = 4$ cm^2 mol^{-1} ohm^{-1}) and is monomeric in $CHCl_3$. The crystalline mononitrosyl complex is stable at room temperature in a dry atmosphere. It is soluble in many organic solvents including alcohol, acetone, chloroform, and benzene to give deep reddish brown solutions although relatively rapid decomposition occurs on standing (see below). Attempts to prepare the five-coordinate complex by reaction of solid $Co(SacSac)_2$ with excess liquid NO were unsuccessful. Although a reaction occurs, the desired complex could not be isolated.

Comparison of the infrared spectrum (Table II) with that of $Co(SacSac)_2$[13] confirms the presence of coordinated NO by the characteristic strong band at 1649 cm^{-1} (KBr disk). The sulfur ligand appears to be chelated in the usual manner with the C$\cdots$C stretching mode decreasing slightly from 1490 cm^{-1} in $Co(SacSac)_2$ to 1480 cm^{-1} in the nitrosyl complex. A larger decrease to 1460 cm^{-1} is observed with the tris chelate $Co(SacSac)_3$.[10,14] Since the new compound appears to contain no unpaired electrons (see below), it may be regarded formally as containing the NO^- ion coordinated to Co(III), attained by electron transfer from Co(II) to NO. Similar oxidations of $Co(SacSac)_2$ have been characterized with a range of bidentate ligands.[10,11] The ν(N–O) frequency is compatible with coordinated NO^- and similar to the ν(N–O) stretching energy of 1626 cm^{-1} observed in $Co(NO)(S_2CN$-

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Table I. Analytical and General Data

		% C		% H		% Co		% N		% S		Mol wt[a]	
Compd	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Co(NO)_2(SacSac)$	Red-brown	24.0	24.5	2.8	3.4	23.6	23.7	11.2	10.4[b]	25.6		250	260
$Co(NO)(SacSac)_2$	Dark brown	34.2	34.1	4.0	3.9	16.8	17.3	4.0	3.7	36.5	36.6	351	351

[a] By vapor pressure osmometry in $CHCl_3$ at 25°. [b] N values for several preparations span the range 9.6–12.2%.

Table II. Infrared Spectral Data (KBr Disk; 2000–300 cm^{-1})

$Co(SacSac)_2$	$Co(NO)(SacSac)_2$	$Co(NO)_2(SacSac)$	Assignment[a]
	1649	1820 1750	ν(N–O)[b]
1490	1480 br	1480	ν(C–C) + δ(C–H)
1356	1360	1360	CH_3 def
1344	1345	1335	ν(C–C)
1313 1288	1311 1290	1316 1292	C–H in-plane bend
1157	1159	1150	$\nu(C–CH_3)$
1006	1010 br	1009 br	CH_3 rock
842	841		
	828	820	C–H out-of-plane bend
745	745	747	ν(C–S) + $\nu(C–CH_3)$
700	702	698	ν(C–S)
548	550	552	$\nu(C–CH_3)$ + ring def
	490	508	ν(Co–N) or δ(Co–N–O)
374	371[c]	352	ν(Co–S)
	362[c]	321	ν(Co–S)

[a] Assignments for Co(SacSac) moiety from normal-coordinate analysis of $Co(SacSac)_2$.[13] [b] Solution spectra of ν(N–O) bands: $Co(NO)(SacSac)_2$, CH_2Cl_2, 1665 cm^{-1}; $Co(NO)_2(SacSac)$, CH_2Cl_2, 1830, 1769 cm^{-1}; *n*-hexane, 1827, 1769 cm^{-1}. [c] CsI disk.

$Me_2)_2$. The stereochemistry of the new compound is expected to be based on the five-coordinate rectangular-based pyramidal geometry established[7] for $Co(NO)(S_2CNMe_2)_2$ with a nonlinear Co–N–O bond.[3,7b]

The mononitrosyl complex exhibited a residual magnetic moment of 0.66 BM at room temperature which decreased to 0.48 BM when the temperature was lowered to 156°K. In fact, the magnetic moment varies linearly with $T^{1/2}$ consistent with the presence of temperature-independent paramagnetism (186×10^{-6} cm^3 mol^{-1}) which is also observed for the mononitrosyl of *N,N'*-ethylenebis(salicylideniminato)-cobalt(II).[15] Such a TIP term is characteristic of the low-spin d^6 configuration[16] and may promote broadening of nmr lines of the mononitrosyl by decreasing the relaxation times.[17] In fact, the complex exhibits a proton nmr spectrum in the expected region for diamagnetic complexes of dithioacetylacetonate (Table III) and the peaks are unusually broad (Figure 1).

Although a small amount of paramagnetic $Co(SacSac)_2$ impurity may be responsible for the line broadening, similar explanations are unlikely to account for the broad spectra observed by Fay and Piper[17] for β-diketonate complexes of Co(III). Quadrupolar relaxation by ^{59}Co, particularly in the low symmetry of the five-coordinate complex, may also account for the observed broadening of the nmr signals.[18]

$Co(NO)_2(SacSac)$. This complex is formed to some extent during the low-temperature reaction to form $Co(NO)(SacSac)_2$ although it is obtained in better yield from reaction of $Co(SacSac)_2$ with NO at room temperature. Although the dinitrosyl is more stable in solution than $Co(NO)(SacSac)_2$, its extreme solubility in all solvents including petroleum ether, *n*-pentane, and alcohols prevents the usual recrystallization procedures from being employed. Rapid evaporation of the solvent affords acceptably pure samples although a small proportion of the "crystallized" compound will not redissolve in *n*-pentane at each recovery step.

Table III. Nmr Data in $CDCl_3$ Solution

	Chem shift[a]		
Compd	CH_3	C–H	Area ratio
$Co(NO)(SacSac)_2$	~2.58	~7.35	*b*
$Co(NO)_2(SacSac)$	2.60	7.37	6:1
$Co(SacSac)_3$[c]	2.32	6.85	6:1
$Ru(NO)Cl(SacSac)_2$[d]	2.63	7.13	6:1

[a] δ (ppm) with reference to TMS. [b] Apparently 6:1 although residual $CHCl_3$ peak interferes; peaks quite broad; *cf.* Figure 1. [c] Reference 10. [d] G. A. Heath, Ph.D. Thesis, University of Melbourne, 1970.

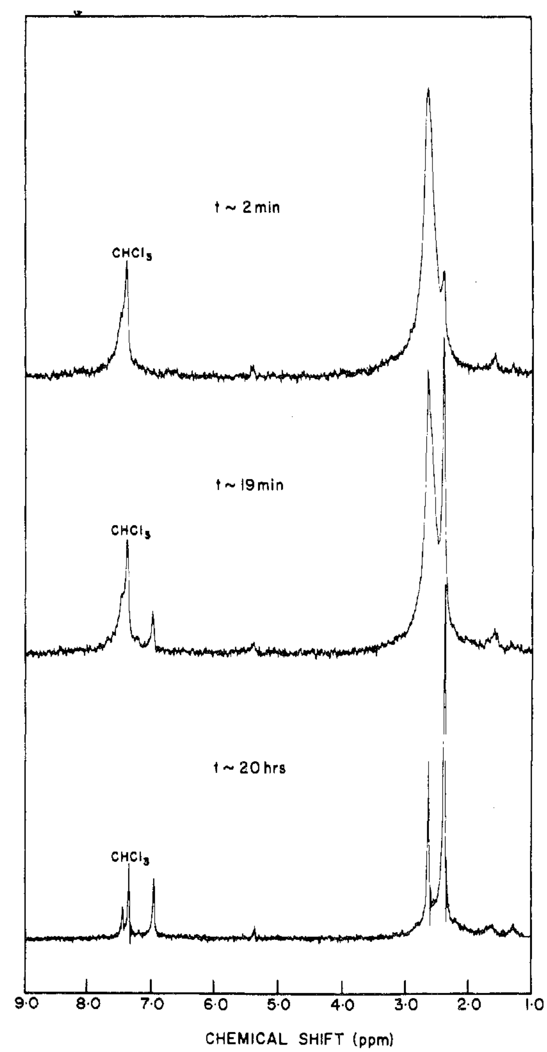

Figure 1. Time dependence of the nmr spectrum ($CDCl_3$) of $Co(NO)(SacSac)_2$, illustrating its ready conversion to $Co(NO)_2(SacSac)$ (δ 2.60, 7.37 ppm) and $Co(SacSac)_3$ (δ 2.32, 6.85 ppm) at ambient temperatures. Instrument gain is different for each spectrum.

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The complex is monomeric in $CHCl_3$ solution (Table I) and is a nonelectrolyte in nitromethane as evidence by a molar conductance of 3 $cm^2\ mol^{-1}\ ohm^{-1}$.

The infrared spectrum (Table II) clearly indicates the presence of chelated $SacSac^-$ and coordinated nitrosyl groups. The observation of two bands in the ν(N–O) region at 1750 and 1820 cm^{-1}, taken together with the monomeric nature of the complex, suggests the cobalt ion is either square planar or tetrahedrally coordinated. If it is inferred from the ir evidence that the nitrosyl is linearly bound (*i.e.*, NO^+), then it would be expected that the formally Co^- species is pseudotetrahedrally coordinated. The diamagnetism of the complex (nmr evidence) accords with this prediction. One band in the spectrum of $Co(NO)_2(SacSac)$ not observed in the ir spectrum of $Co(SacSac)_3$ or $Co(SacSac)_2$ lies at 508 cm^{-1}. Cleare and Griffith,[19] on the basis of ^{15}N substitution studies on nitrosyl complexes, suggest bands in this region are either ν(M–N) or δ(M–N–O) in origin. Similarly, an extra band (590 cm^{-1}) is also observed in the spectrum of $Ru(NO)Cl(SacSac)_2$.[4]

The nmr spectrum (Table III) confirms that the ligand has not undergone nitrosylation. The chemical shift values for the new complex are downfield from the values observed with all the simple transition metal dithioacetylacetonates recorded to date. Interestingly, the resonances are in the same region as those of the d^{10} presumed tetrahedral complex $Zn(SacSac)_2$ (CH_3, 2.52 ppm; H, 7.27 ppm).

The mass spectra of both the new compounds present NO^+ (*m/e* 30) as the most abundant ion. For the dinitrosyl the parent ion $Co(NO)_2(SacSac)^+$ is observed as are fragments corresponding to successive loss of nitric oxide, *i.e.*, $Co(NO)_2(SacSac)^+$ (*m/e* 250), $Co(NO)(SacSac)^+$ (*m/e* 220), and $Co(SacSac)^+$ (*m/e* 190). In contrast, the parent ion is not observed in the mass spectrum of the mononitrosyl either at low (20°), intermediate, or high (80°) probe temperatures, possibly due to instability of either the mononitrosyl or the parent ion $Co(NO)(SacSac)_2^+$. Certainly the spectrum of the mononitrosyl contains peaks directly attributable to $Co(NO)_2(SacSac)$ fragments (*m/e* 250, 220, 190), which is consistent with decomposition of the mononitrosyl. Ions at *m/e* 321 and 131 are assigned to $Co(SacSac)_2^+$ and the 3,5-dimethyl-1,2-dithiolium ($C_5H_7S_2^+$) ions, respectively. Although both ions dominate the spectra of $Co(SacSac)_2$[20] and $Co(SacSac)_3$,[10,14] they might also arise from direct fragmentation of $Co(NO)(SacSac)_2^+$.

Disproportionation of $Co(NO)(SacSac)_2$. $Co(NO)(SacSac)_2$ is unstable in solution and spontaneously decomposes at room temperature. This process can be readily followed by ir (NO aspect) and nmr techniques (proton aspect).

A rapidly prepared solution of $Co(NO)(SacSac)_2$ in CH_2Cl_2 exhibits an N–O stretching frequency at 1665 cm^{-1}, shifted only slightly from the value observed in a KBr matrix (1649 cm^{-1}). This peak steadily decreases in intensity over a few hours and is replaced by two new peaks growing uniformly at 1769 and 1830 cm^{-1} (Figure 2), which are identical in position and intensity ratio with those observed for a pure sample of $Co(NO)_2(SacSac)$.

Nmr spectroscopy establishes the presence of two products and the ratio in which they are formed. As the decomposition proceeds, the broad nmr signals of $Co(NO)(SacSac)_2$ are steadily replaced by new peaks (Figure 1) which can be unambiguously assigned to $Co(NO)_2(SacSac)$ and $Co(SacSac)_3$. Integration of peak areas establishes that these two products are formed in a 1:1 ratio which is consistent with a disproportionation reaction of the stoichiometry

$$2Co(NO)(SacSac)_2 \rightarrow Co(NO)_2(SacSac) + Co(SacSac)_3$$

The mechanism of this reaction remains unknown and will require a detailed kinetic study for its elucidation. The overall stoichiometry raises the interesting possibility that association to a bimolecular transition state (Figure 3) involving octahedrally coordinated cobalt might be involved. However, reasonable dissociative mechanisms can also be formulated.

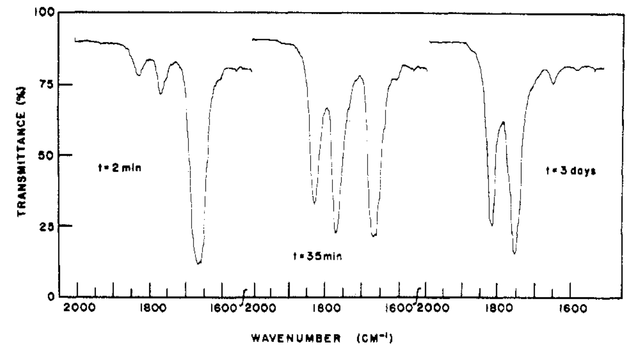

Figure 2. Infrared spectrum (CH_2Cl_2) of $Co(NO)(SacSac)_2$ (1665 cm^{-1}) illustrating its conversion to the dinitrosyl, $Co(NO)_2(SacSac)$ (1830 and 1769 cm^{-1}). Spectra are compensated for solvent absorption. Final spectrum (t = 3 days) was obtained on a more dilute solution than the first two spectra (t = 2 and 35 min).

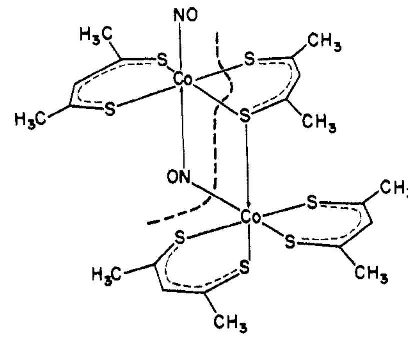

Figure 3. Possible binuclear intermediate affording conversion of $Co(NO)(SacSac)_2$ to $Co(NO)_2(SacSac)$ and $Co(SacSac)_3$.

Registry No. $Co(SacSac)_2$, 36869-01-9; $Co(NO)(SacSac)_2$, 50986-65-7; $Co(NO)_2(SacSac)$, 50986-66-8.

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