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Synthesis and Characterization of a Paramagnetic $\{CoNO\}^7$ Complex: Bis-*o*-Phenylenebis(dimethylarsine)chloronitrosylcobalt Diperchlorate

BEN T. HUIE, PATRICK BRANT and
ROBERT D. FELTHAM

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA

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A large number of cobalt nitrosyl complexes have been prepared and characterized [1–3] but thus far, all those which have been reported are diamagnetic. Here, we report the synthesis and properties of the first paramagnetic cobalt nitrosyl complex. Passage of dry Cl_2 through a deoxygenated solution of $[Co(NO)(das)_2][ClO_4]_2$* in methanol produces a green precipitate, $[Co(NO)(das)_2Cl][ClO_4]_2$ (I):

$$[Co(NO)(das)_2][ClO_4]_2 + Cl_{2(g)} \xrightarrow{CH_3OH} [Co(NO)Cl(das)_2][ClO_4]_2$$

The infrared spectrum of this green complex exhibits a strong band at 1760 cm^{-1} (KBr) which shifts to 1705 cm^{-1} in the ^{15}N derivative. Accordingly, this band is assigned to ν_{NO}. Elemental analyses are consistent with the formulation of the green complex as (I). Comparison of the X-ray powder patterns of (I) and *trans*-$[Fe(NO)(das)_2Cl][ClO_4]_2$ indicates that the compounds are isomorphous. Thus, (I) is monomeric with *trans* coordination geometry [4].

Both the magnetic susceptibility and ESR spectrum were obtained for (I). The magnetic moment of 1.90 B.M. at 300 °K found for (I) is within the range (1.80–2.23 B.M.) observed for the closely related das complexes of the $\{FeNO\}^7$ group [5]. X-band ESR spectra of (I) were obtained at 77° K for the pure solid and for a CH_2Cl_2 glass. The ESR spectra of both the solid and glass consisted of a single broad asymmetric line (FWHM 119–138 G) with $g_{\langle ave \rangle}$, 1.985 ± 0.005. The ESR spectra of the ^{14}NO and ^{15}NO derivatives were examined. A small decrease was observed in the line width of the ^{15}N complex, but no hyperfine splitting could be resolved. The line widths found for the ESR spectra of (I) are significantly less than the 500 G expected for unresolved ^{75}As hyperfine splitting [6], and more closely correspond to that of *ca.* 200 G expected for overlapping components of the g tensor with unresolved ^{14}N hyperfine splitting [7]. The asymmetry of the ESR spectrum indicates that the g tensor has the tetragonal or rhombic symmetry normally found for six-coordinate $\{FeNO\}^7$ complexes [7, 8].

Although the information cited above does not provide any direct information about the CoNO bond angle, the similarity between the physical properties of (I) and the six-coordinate $\{FeNO\}^7$ complexes all of which are known to have significantly bent FeNO groups [4, 9, 10] suggests that the CoNO group is not linear. Assuming that the CoNO group of (I) is bent, the complex has C_s symmetry and should have an electronic structure closely related to that of the $\{CoNO\}^8$ complex, *trans*-$[Co(NO)(das)_2Cl][ClO_4]$, (II), [11, 12]. The HOMO of (II) consists of two electrons in the $2a'(\Pi_x^*(NO), xz)$ orbital [11, Fig. 7]. Removal of one electron from this orbital should result in a $\{CoNO\}^7$ complex with one unpaired electron in the $2a'$ orbital and a $^2A'$ electronic ground state similar to the $\{FeNO\}^7$ group [13].

To further elucidate the electronic properties of (I), X-ray photoelectron spectra of (I), (II) and *trans*-$[CoCl_2(das)_2][ClO_4]$, (III), were obtained and are summarized in the Table. Within experimental error (± 0.3 eV) the Co $2p_{3/2}$ binding energies of (II) and (III) are identical, consistent with the formulation of (II) as a derivative of Co(III) [1]. Oxidation of (II) to (III) results in an increase of both the Co $2p_{3/2}$ and N 1s binding energies. However, the 1.4 eV increase in the N 1s binding energy is greater than the 0.7 eV increase observed for the Co $2p_{3/2}$ level. These results are consistent with the molecular orbital scheme outlined in [11], in which the HOMO of (II) is a molecular orbital in the plane of the CoNO group localized primarily on the nitrogen atom. Oxidation of (II) results in the removal of one electron from this HOMO with a decrease in electron density on the nitrogen atom and a concomitant increase in the N 1s binding energy. This HOMO also has a component from the d_{xz} orbital of the metal, so that some increase in the Co $2p_{3/2}$ binding energy is not unex-

TABLE. ESCA Spectra.

Compound	Binding Energies, eV[a]	
	Co $2p_{3/2}$	N 1s
(I) $[Co(NO)(das)_2Cl][ClO_4]_2$	781.8(1.8)[b]	402.5(2.1)
(II) $[Co(NO)(das)_2Cl][ClO_4]$	781.1(2.2)	401.1(1.9)
(III) $[CoCl_2(das)_2][ClO_4]$	781.0(2.1)	–

[a] All binding energies are standardized to the C 1s peak at 285.0 eV of the das ligands. [b] Values in parentheses are peak full width at half maximum values, in eV.

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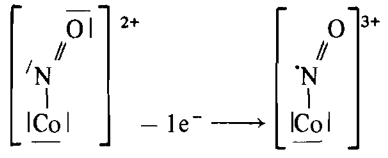
*das is *o*-phenylenebis(dimethylarsine).

pected. However, there is little or no contribution from the orbitals of the arsenic ligand to the HOMO, and consequently no change in the As 3d binding energy was expected and none was observed.

In a *formal sense* then, the oxidation of (II) to (I) can be described as the oxidation of coordinated $(\langle\mathrm{N{=}O}\rangle)^-$ to coordinated $(\langle\dot{\mathrm{N}}{=}\mathrm{O}\rangle)^0$:



The XPS spectrum of (I) also supports this view. Normally paramagnetic cobalt complexes exhibit satellites in the Co 2p region while the ligands attached to these paramagnetic cobalt centers do not [15]. The results obtained for (I) contrast with those obtained for other paramagnetic cobalt complexes: no satellites were observed in the Co 2p region and the N 1s peak is broad and skewed toward high binding energies. Deconvolution of this N 1s peak into two peaks with enforced area ratios of 1:2 led to two peaks separated by 1.0 eV each with FWHM of 1.7 eV. Photoionization of a N 1s core electron from (I) will lead to singlet and triplet ionized states of different energies. In free NO [16], these two states are separated by 1.4 eV, compared with the 1.0 eV determined for (I). Since the extent of the energy separation of the singlet and triplet states is directly proportional to the extent of localization of unpaired density on the NO group, the broadened N 1s spectrum of (I) is consistent with the molecular orbital description and with the conclusion that the unpaired electron density in (I) largely resides on the nitrosyl group.

Finally, oxidation of (II) to (I) results in an increase of 100 cm^{-1} in ν_{NO} which also corresponds to removal of electron density from the NO groups. It is hoped that more detailed structural information can be obtained from X-ray structural studies, but our attempts to prepare suitable single crystals of (I) have thus far failed.

Experimental

All reactions were carried out in Schlenkware using dry deoxygenated solvents in an N_2 atmosphere. The IR spectra were obtained from KBr pellets using a Beckman IR 12 spectrometer. The ESR spectra were obtained with a Varian model E3 operating at approximately 9.5 GHz. The photoelectron spectra were obtained from powdered samples mounted on double-stick tape at −95 °C using a McPherson ESCA 36 spectrometer. The binding energies reported were standardized using a C 1s binding energy of 285.0 eV for the das ligand [14]. The elemental analyses were performed by Chemalytics Inc., Tempe, Arizona. The magnetic susceptibility was determined by the Faraday method. Anal. Calculated for $C_{20}H_{32}NO_9Cl_3As_4Co$: C, 26.83; H, 3.60; N, 1.56; Cl, 11.88. Found: C, 27.03; H, 3.33; N, 1.42; Cl, 11.50. Compounds (II) and (III) were available from studies previously described [11].

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