as already suspected from solid-state EPR measurements.[8] Recent calculations[19] of the Cu(I)–Cu(I) interactions in a polynuclear complex demonstrate that, when the orbitals s, p, and d of each of the two Cu(I) are considered, the positive (i.e., attractive) mutual interaction of the coppers almost vanishes as soon as their distance exceeds 3.5–4 Å. It is therefore reasonable to expect the Cu(I)–Cu(I) interactions to be weak in the reduced form of **1**.

The second argument may support the occurrence of a very weak coupling between the two Cu(II) in **1**. This results from the shape of the cyclic voltammograms and from the analysis of the stationary reduction wave on a platinum rotating disk electrode. Several years ago, the theoretical analysis of the peaks in cyclic voltammetry has been developed[20] for two fast, monoelectronic, simultaneous or quasi-simultaneous reduction steps; when the redox step is neither unique nor really bielectronic (i.e., $E_2^\circ - E_1^\circ$ being not > 0), then the difference between the peak and the half-peak reduction potentials ($E_p - E_{p/2}$) exceeds 29 mV. In dinuclear complex **1** this difference is 51 ± 2 mV, which corresponds[20] to a difference $E_2^f - E_1^f = -27 \pm 3$ mV between the formal redox potentials of the two coppers (E_2^f corresponds to the second monoelectronic step). With totally uncoupled Cu(II) centers in the complex, this difference $E_2^f - E_1^f$ would be -35.6 mV at 298 K.[13,14] These cyclic voltammetry results are complemented by the slope (57 ± 2 mV) of the log plot (Figure 2) of the cathodic wave recorded on a rotating disk electrode; the reduction is fast on the time scale of the measurements, the slope 57 ± 2 mV being almost that expected[14] for a process involving two independently reduced redox centers (59.1 mV). With this value of 57 ± 2 mV, the calculated[13] difference $E_1^f - E_2^f$ is equal to 32 ± 4 mV, in agreement with the value 27 ± 3 obtained above from cyclic voltammograms. Thus, the experimental value of $E_1^f - E_2^f$ may be given as 30 ± 6 mV,[21] which is close to the 35.6 mV corresponding to the absence of interactions between the two coppers, taking into account the uncertainty of the potential measurements.

The present results are fully consistent with the reduction of the two copper(II) in cryptate **1** via two monoelectronic steps, each step involving a distinct Cu(II) center. Thus $E_0 = +200 \pm 11$ mV/SCE for each of the two Cu(II)/Cu(I) couples in **1**, the two Cu(II) being almost noninteracting.

Thus, dinuclear cryptate **1** may be considered as a *dielectronic receptor* unit, which might be able to exchange two electrons in a single encounter. It represents a prototype for the study of cooperativity between two (or more) sites in electron-transfer processes and for catalysis of reactions requiring the transfer of several electrons. Furthermore the redox properties of the dinuclear complex **1** (markedly positive standard potential and fast two-electron acceptor/donor system) mimic type 3 copper sites in copper proteins.[6]

Apart from the known effect of the macrocyclic ligand to weaken the interaction of the coppers with the surrounding medium, the unusual redox properties of complex **1** may be ascribed to the following factors: (i) The moderately positive potentials (compared to polythiamacrocycles[7,23]) arise from the chemical nature of the coordination sites (two nitrogen and only two sulfurs) as well as from the coordination stereochemistry which is intermediate between square planar and tetrahedral.[8] (ii) The ability of the cryptate to function as a

"cascade-like" two-electron-transfer site results from the intercationic distance imposed by the structure of the ligand.[24]

Modifying the length of the side-branches which connect the two monocycles in the macrotricyclic ligand (Figure 1a) does not affect[25] qualitatively the general redox behavior of the dinuclear copper complex, provided their length remains large enough to prevent significant coupling between the two coppers.

Registry No. 1, 67340-45-8; **1**, reduced form, 72925-69-0.

(24) The opening of one of the side-branches in the cryptand (Figure 1a), as it suppresses this structural control, should allow various conformations. In such dinuclear copper complexes, the above results lead one to expect qualitatively analogous redox behavior with, however, a probable slowdown of the overall rate of the two-electron transfer.[22]

(25) J. P. Gisselbrecht and M. Gross, to be submitted for publication.

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Photoelectron Spectra of Nitrosyldicarbonyl(η^5-cyclopentadienyl)chromium and Thionitrosyldicarbonyl(η^5-cyclopentadienyl)chromium. Comparison of the Electronic Structures of Metal–NO and Metal–NS Complexes

John L. Hubbard and Dennis L. Lichtenberger*

Legzdins and Kolthammer recently reported the preparation and structure of the first organometallic thionitrosyl complex, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NS$ (I).[1,2] This complex is isoelectronic and basically isostructural with a large group of $(\eta^5\text{-}C_5H_5)M(CO)_2L$ complexes, where L is a small molecule or fragment species. We have found that such complexes are highly useful for providing detailed information on the relative bonding and electronic interactions between the metal and the attached ligand.[3–6] Our approach combines high-resolution study of the valence ionizations of the complex in the gas phase with appropriate theoretical calculations. It is useful to compare the thionitrosyl complex with the corresponding nitrosyl complex, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (II), and the isoelectronic and basically isostructural manganese carbonyl and thiocarbonyl complexes, $(\eta^5\text{-}C_5H_5)Mn(CO)_2CS$ (III) and $(\eta^5\text{-}C_5H_5)Mn(CO)$ (IV). It follows from the results of our similar study on complexes III and IV[4] that NS should be a better π-accepting ligand than NO, which is interesting since NO is already considered to be a strong π acid. Another very important feature should be the greater interaction of the filled NS orbitals with the metal electrons.

The nitrosyl[7] and thionitrosyl[1] complexes were prepared and purified by published procedures. Spectra were measured on a McPherson ESCA 36 spectrometer fitted with the He I source chamber and a temperature-controlled sample ionization chamber of our own design (I, 25 °C; II, 45 °C). Dis-

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(21) With the assumption of equal (fast) rate constants for the two monoelectronic steps, this difference corresponds[22] to a thermodynamic dismutation constant K of about 0.3 for the mixed complex (Cu(II),Cu(I)). [$K = (2Cu^{II} \text{ligand})(2Cu^I \text{ligand})/(Cu^{II}, Cu^I \text{ligand})^2$].

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(2) T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter, *J. Chem. Soc., Chem. Commun.*, 1036 (1978).

(3) D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, **98**, 50 (1976).

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(5) D. L. Lichtenberger and R. F. Fenske, *J. Organomet. Chem.*, **117**, 253 (1976).

(6) B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979).

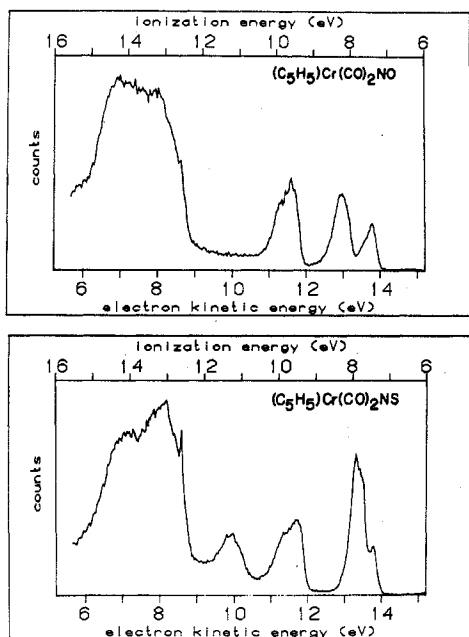(7) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).

Figure 1. Helium I valence photoelectron spectra of $(\eta^5\text{-}C_5H_5)$Cr-$(CO)_2$NO and $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NS.

played spectra are the time-averaged result of individual scans of ~200-s duration. Instrument drift was controlled at less than 0.005 V, and resolution was less than 0.030 V fwhm for the Ar $^2P_{3/2}$ line throughout data acquisition. Parameter-free molecular orbital calculations were performed according to the method of Fenske and Hall[7] for idealized geometries[8] based on the crystal structures of the nitrosyl[9] and thionitrosyl[2] complexes.

The valence photoelectron spectra of the nitrosyl and thionitrosyl complexes are shown in Figure 1. The major ionization features are easily assigned from comparison with the spectrum of $(\eta^5\text{-}C_5H_5)$Mn$(CO)_3$ and other systems from our previous studies.[3-5] The bands between 7 and 9 eV are associated with ionization from orbitals that are primarily metal d in character. Although we have observed metal–ligand vibrational fine structure in the metal ionizations of some carbonyl complexes,[10] we have not yet been able to obtain well-defined vibrational structure in the metal ionizations of these chromium complexes. These vertical ionization energies are very sensitive to the substitution at the metal center (vide infra). The ionization band between 9 and 10 eV in each spectrum corresponds to the cyclopentadienyl e_1'' orbitals that donate density into empty metal d orbitals. These bands have the characteristic shoulder on the high ionization energy side that we always observe for this ionization.[3-5] Both spectra have a broad, intense structure between 12 and 16 eV due to the carbonyl 5σ and 1π ionization and certain $\eta^5\text{-}C_5H_5$ ionizations. The nitrosyl 5σ and 1π ionizations are presumed to be in this area also. The spectrum of the thionitrosyl complex has an additional broad band between 11 and 12 eV that is well separated from the other ionizations of the complex. A similar

(8) The geometry of the $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$ portion of the molecules was the same for the $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NO and $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NS calculations. The geometry of the cyclopentadienyl ring was the same as that used in ref 4. The distances from the metal to the other atoms are from the crystal structures, and the L–Cr–L' angles were constrained to 90° (L = carbonyls, nitrosyl, or thionitrosyl). The usual chromium (+1) functions were used[7] with 4s and 4p exponents of 2.0 and 2.1, respectively.

(9) J. L. Atwood, R. Shakir, J. T. Malito, M. Herberhold, W. Kremnitz, W. P. E. Berhagen, and H. G. Alt, *J. Organomet. Chem.*, **165**, 65 (1979).

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Table I. Calculated Eigenvalues (eV)^a

primary character	CpMn(CO)$_3$^{b}	CpCr(CO)$_2$NO	CpCr(CO)$_2$NS
metal d	−9.35 (e)	−8.94 (2a')	−8.82 (2a')
		−10.01 (a'')	−9.18 (a'')
	−9.48 (a$_1$)	−10.01 (1a')	−9.29 (1a')
Cp e_1''	−13.52	−12.52	−12.30
	−13.57	−12.57	−12.45

^{a} Symmetry labels are in parentheses; see ref 6. ^{b} From ref 3.
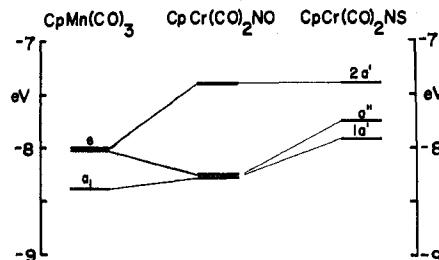
Figure 2. Changes in ionization energies from $(\eta^5\text{-}C_5H_5)$Mn$(CO)_3$ to $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NO and $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NS. The symmetry labels indicate the energies that change as indicated by the calculations. See also ref 3 and 6.

situation occurred in the case of $(\eta^5\text{-}C_5H_5)$Mn$(CO)_2$CS, in which ionizations from the CS σ-donor orbital to the metal and the CS π bond occurred in this region. Further experimental work is presently under way to definitively determine the nature of ionization in this region of the $(\pi^5\text{-}C_5H_5)$Cr-$(CO)_2$NS spectrum.

The calculated eigenvalues of the valance molecular orbitals of these complexes are given in Table I. Of course, it is not to be expected that these eigenvalues will correspond directly to the vertical ionization energies because of the well-known limitations of Koopmans' approximation[11] and because of the limitations of the approximate method used. However, these complexes are related to each other in specific, well-defined ways such that the changes in ionization energies from one complex to the other will be largely reflected in the changes in the eigenvalues.[12] For instance, $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NO is related to $(\eta^5\text{-}C_5H_5)$Mn$(CO)_3$ by one less proton at the metal atom and one more proton at the bound ligand atom. The thionitrosyl complex is related to the nitrosyl complex by the less electronegative and larger sulfur atom in place of the oxygen atom. The point of interest is observation of how the primarily metal and cyclopentadienyl ionizations are perturbed by these changes in the molecular complex.

Figure 2 shows the changes in the primarily metal ionization energies from $(\eta^5\text{-}C_5H_5)$Mn$(CO)_3$ to the Cr–NO and –NS compounds. The calculated eigenvalues and the observed ionization energies show several similar trends. The ionizations of $(\eta^5\text{-}C_5H_5)$Mn$(CO)_3$ which correspond to the e and a$_1$ orbitals are calculated to be close in energy and are not resolved as separate bands in the spectrum, as discussed in detail previously.[3] The calculation on $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NO indicates that a single ionization should occur at about 1 eV lower binding energy than two essentially degenerate ionizations, and this is clearly observed in the 1:2 intensity pattern in the ionizations between 7 and 9 eV (Figure 1). The metal ionizations of $(\eta^5\text{-}C_5H_5)$Cr$(CO)_2$NS are calculated to be grouped more closely together than the corresponding ionizations of the nitrosyl complex, although the second and third levels are not so closely degenerate. The closer grouping of the ionizations is clearly seen in Figure 1, and in fact the second ionization is partially resolved from the third as a shoulder

(11) W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).
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Table II. Populations of CO, NO, and NS σ-Donor and π-Acceptor Orbitals and Atomic Charges

	CpMn(CO)₃		CpCr(CO)₂NO		CpCr(CO)₂NS	
		Orbital Populations				
CO 5σ	1.42	CO 5σ	1.49	CO 5σ	1.51	
CO 2π	0.62	CO 2π	0.57	CO 2π	0.52	
		NO 5σ	1.58	NS 7σ	1.61	
		NO 2π	1.50	NS 3π	1.69	
		Atomic Charges				
Mn	+0.42	Cr	+0.80	Cr	+0.87	
C(CO)	+0.02	C(CO)	−0.10	C(CO)	−0.09	
O(CO)	−0.06	O(CO)	+0.02	O(CO)	+0.05	
		N(NO)	+0.03	N(NS)	−0.25	
		O(NO)	−0.09	S(NS)	+0.04	

of the intense metal band at 8 eV.

The significance of the metal ionizations of these $(\eta^5\text{-}C_5H_5)M(CO)_2L$ systems can be appreciated if the basic orbital structures of the $(\eta^5\text{-}C_5H_5)M(CO)_2$ and L fragments are understood. We recently presented the analysis of $(\eta^5\text{-}C_5H_5)M(CO)_2$ in detail.[6] Briefly, the three occupied metal orbitals in the d^6 $(\eta^5\text{-}C_5H_5)M(CO)_2$ fragment are labeled 1a', 2a', and a''. The 1a' and a'' are effective π donors to the ligand (L), a'' being the best donor. The 2a' orbital is largely δ symmetry with respect to the ligand and will mostly reflect the effects of total charge distribution around the metal.

It is observed (and calculated) that the ionization energy of 2a' decreases dramatically in going from the Mn to the Cr compounds, consistent with going from formally Mn⁺ to Cr⁰. As mentioned, the relationship between the Mn and Cr complexes can be thought of as the transfer of a proton from the metal to the ligand, while a d^6 configuration is retained around the metal. The electrons in the immediate vicinity of the chromium lose some of the stabilizing influence of the proton.[13] The 1a' and a'' also experience this effect but in addition are stabilized by the better π-accepting ability of NO (and NS). The calculated Mulliken populations of the π*-acceptor orbitals of CO, NO, and NS in these three molecules are given in Table II. The a'' orbital is influenced slightly more than the 1a' by changes in π bonding because of its greater π interaction. It is interesting that, for the corresponding orbitals of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, the a'' is less stable than the 1a', while the calculations indicate that these orbitals are essentially degenerate for the nitrosyl complex, as is observed in the ionizations. In a sense the electronic symmetry axis for the metal has shifted from the direction of the cyclopentadienyl ring centroid in the manganese complex to the direction of the nitrosyl ligand in the chromium complex.

The comparison of NO and NS orbital interactions with the metal is shown in the molecular orbital diagram in Figure 3. The differences in electronic structure between the two complexes are influenced more substantially by the ligand-orbital energies than by orbital overlaps. Just as in our previous comparison of CS with CO, the π* orbital of NS is lower in energy than the π* of NO (weaker $p_\pi\text{-}p_\pi$ bonding for sulfur compared to oxygen) and accepts more electron density from the metal. A surprising feature of Figure 2 is that, even though the electronic interactions of NS and NO are appreciably different, the ionization associated with the 2a' orbital does not significantly shift from the nitrosyl to the thionitrosyl complex. The calculations agree with this observation and indicate that stabilization caused by removal of metal electron density by π back-bonding to NS is offset by the greater electron density on nitrogen (sulfur is less electronegative than oxygen) and decreased metal back-bonding to the carbonyls.
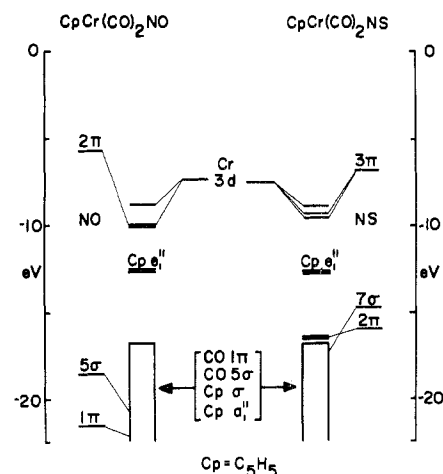
Figure 3. Molecular orbital diagrams (Fenske–Hall method) for $(\eta^5\text{-}C_6H_5)Cr(CO)_2NO$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2NS$ emphasizing relative energy comparisons of NO and NS orbital interactions with the metal orbitals.

Another observation from Figure 2 is that the 1a' and a'' ionizations of the thionitrosyl complexes are actually at lower ionization energy than for nitrosyl complex. This seems surprising on the basis of the better π-acceptor ability of NS compared to that of NO. The explanation is the same as in our comparison of CS and CO. The decreased π interaction between the nitrogen and sulfur greatly destabilizes the NS π bond, which then interacts more strongly with the filled metal 1a' and a'' orbitals. This interaction will tend to again separate the 1a' and a'' ionizations, and, indeed, this separation is partly resolved in the photoelectron spectrum. In terms of the ionizations, the greatest difference between the NS and NO compounds is the interaction of their π bonds with the metal. As in the case of CO and CS, this will also have an important influence on their chemical and physical properties.

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Symmetry of the Lowest Excited States of the Tris(2,2'-bipyridyl)ruthenium(II) Ion

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Solution-phase luminescence and excited-state electron-transfer processes associated with the Ru(bpy)₃²⁺ ion have made it the object of intense electro- and photochemical study. Despite the hundreds of papers in the literature concerning this ion, there is still no universally accepted assignment of the luminescence. This communication will address the assignment of the luminescence from the standpoint of its polarization. We find that our single-crystal polarized emission data are inconsistent with some of the assignments which have been proposed. Further, we find an interesting anomaly in the photoselection spectra of this complex in rigid matrices that suggest an excited-state and/or ground-state molecular symmetry which is lower than D_3. These conclusions are *not based on any choice of model.*

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(13) This is reflected in the diagonal Fock matrix elements for the metal orbitals but not necessarily in the metal charges in Table II because of the accompanying interflow of electron density with neighboring atoms.