

the very high C–O stretching frequencies, increase with decreasing counter anion basicity. Even though a molecular structure of this compound was not obtained, the careful analysis of the complete vibrational spectrum of the cation with the aid of ^{13}C and ^{18}O isotope substitution has allowed a normal coordinate analysis and valence force field calculations, which permit good structural insights.

The unusual bonding situation is seen as a manifestation of drastically diminished metal-to-ligand π -back donation. Trends in stretching force constants for the isoelectronic and isosteric series $[\text{Au}(\text{CN})_2]^-$, $\text{Hg}(\text{CN})_2$, and $[\text{Au}(\text{CO})_2]^+$ suggest that the gradually increasing effective nuclear charge on the metal due to the change in ionic charge is the cause for the gradually decreasing π -back donation in the above series. Consistent with this view is noticeable π -back donation, suggested by the vibrational spectrum of the matrix-isolated neutral $\text{Au}(\text{CO})_2$.¹⁰

It is surprising that the gold–carbon σ bond in $[\text{Au}(\text{CO})_2]^+$ is sufficiently strong to permit isolation of thermally stable compounds. The thermal stability is best explained by the documented ability of gold(I) to form strong covalent, linear bonds,^{1,2} possibly aided by relativistic effects^{62,63} and by polar contributions to the gold–carbon bond, as suggested by the inverse relationship between thermal stability and counter anion basicity observed in this study and discussed above.

The weak gold–carbon bond allows facile replacement of CO by acetonitrile, illustrated by the conversion of $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$ to $[\text{Au}(\text{NCCH}_3)_2][\text{Sb}_2\text{F}_6]$. The structure and bonding features observed for both $[\text{Au}(\text{CO})_2]^+$ and $[\text{Au}(\text{NCCH}_3)_2]^+$ are very similar and apparently determined by the gold(I) center, with its

strict preference for linear coordination, and its ability to form strong covalent bonds in both $[\text{Au}(\text{NCCH}_3)_2]^+$ and $[\text{Au}(\text{CO})_2]^+$. In this respect gold(I) is clearly different even from the other univalent coinage metal ions, a fact best illustrated by the monomeric, linear molecular structure of $\text{Au}(\text{CO})\text{Cl}$ ⁵ and the polymeric structure of $\text{Cu}(\text{CO})\text{Cl}$.⁶⁴ It is also noted that in $\text{Ag}(\text{CO})\text{B}(\text{OTeF}_5)_4$ ²⁴ Ag(I) is tricoordinated. In $[\text{Au}(\text{CO})_2]^+$, carbon monoxide takes the place of an easily interchangeable donor ligand with Au(I) as acceptor. There appears to be no need for the resulting coordination complex to have the nearest noble gas configuration for the central atom, and the effective atomic number rule is irrelevant in this case as in the case of many other group 11 carbonyl derivatives or coordination compounds of univalent gold.^{1,2}

Acknowledgment. Financial support by the North Atlantic Treaty Organization (NATO) (jointly to H.W. and F.A.), by Deutsche Forschungsgemeinschaft (D.F.G.) (to H.W.), and by the Natural Science and Engineering Research Council of Canada (NSERC) (to J.T. and F.A.) is gratefully acknowledged.

Supplementary Material Available: Listing of crystal data, intensity measurements, structure solution and refinement, positional parameters and anisotropic thermal parameters for $[\text{Au}(\text{NCCH}_3)_2][\text{Sb}_2\text{F}_6]$, and intramolecular distances and bond angles, a stereoview of the packing of the molecular ions in the unit cell, and intermolecular contacts out to 3.60 Å with a footnote (9 pages); listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

(62) Pyykko, P. *Chem. Rev.* 1988, 88, 563, and references therein.

(63) Schwerdtfeger, P. *J. Am. Chem. Soc.* 1989, 111, 7261.

(64) Hakansson, M.; Jagner, S. *Inorg. Chem.* 1990, 29, 5241.

Partial Paramagnetism of the Cr–Cr Quadruple Bond

F. Albert Cotton,* Hong Chen, Lee M. Daniels, and Xuejun Feng

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. Received March 30, 1992

Abstract: Variable-temperature NMR measurements show that $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds (L = MeOH, H₂O, py, MeCN) and closely related ones possess inherent, temperature-dependent partial paramagnetism. This may be attributed to a Boltzmann distribution between a ground state with $S = 0$ and a low-lying (~ 400 – 1000 cm^{-1}) state with $S = 1$. When R is kept constant (as CH₃) and the Cr–Cr distance is changed by changing L, the singlet–triplet separation varies inversely with the Cr–Cr distance, suggesting that the low-lying triplet state may be the $^3\text{A}_{2g}$ state arising from a $\sigma^2\pi^4\delta\delta^*$ configuration. Other explanations may also be considered, and cannot be falsified conclusively. The carbamate compound $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4(\text{NEt}_2\text{H})_2$ has also been studied. Despite the fact that the Cr–Cr distance is similar to those in the acetates, the singlet–triplet gap is much smaller, ca. 600 cm^{-1} . This may be attributed to a different interaction of the carbamate ligand with the δ orbital, as is shown by SCF–X α calculations.

Introduction

From the earliest magnetic studies it has been known that $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds display weak paramagnetism in the solid state.¹ There is some evidence to suggest that at least some of this, in at least some cases, is due to the presence of paramagnetic (e.g. Cr(III)) impurities. However, it has also been suggested that the paramagnetism is inherent in the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ molecule owing to the fact that an $S = 1$ state lies within 1000 cm^{-1} of an $S = 0$ ground state. Thus, Furlani² suggested that such

molecules could be regarded as antiferromagnetically coupled systems of two $S = 2$ cores and he used a value of $\chi = 113 \times 10^{-6}$ cgsu at 300 K (and assuming $g = 2$) to get $E = 770\text{ cm}^{-1}$ for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$. The significance of E is indicated by eq 1; it is the separation between the singlet ground state and the lowest triplet state (the S–T gap).

$$\chi = \frac{2Ng^2\beta^2}{3kT} \frac{1}{1 + \frac{1}{3}e^{E/kT}} \quad (1)$$

The use of solid-state magnetic susceptibility data has significant drawbacks. To eliminate the spurious effect of paramagnetic impurities, it is necessary to carry out measurements from room temperature to very low temperatures (ca. 5 K) and then to make

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1992; Chapter 4.

(2) Furlani, C. *Gazz. Chim. Ital.* 1957, 87, 876.

an ad hoc correction. In the case cited above, where low-temperature data were unavailable, the E value obtained can only be considered a lower limit, since the deduction of the contribution made by paramagnetic impurities would give a smaller magnitude for the true paramagnetism of the molecule.

Bilgrien et al.³ have reported the only measurements of the temperature dependence of magnetic susceptibility of $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds, namely $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$, which has a very long Cr–Cr distance (2.541 (1) Å),⁴ and two trifluoroacetate compounds with other axial ligands. After making a correction for a paramagnetic impurity, they fitted their data to eq 1 and obtained a value of $E = 626 \text{ cm}^{-1}$ (with $g = 2.08$). For the two related compounds, whose structures are not known but which must have similar Cr–Cr distances, $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4[\text{OP}(\text{NMe}_2)_3]_2$ and $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4[\text{OP}(\text{OEt})_3]_2$ they obtained E values of 615 and 689 cm^{-1} , respectively.

As we have recently pointed out and illustrated,⁵ in cases where E is in a suitable range (roughly, 500–2500 cm^{-1}) variable-temperature NMR data provide a more convenient and perhaps more accurate way to determine singlet–triplet separations. By measuring the chemical shift(s) of the nuclei in the ligands as a function of temperature for molecules in solution and fitting to an equation that is essentially a modified form of eq 1, one can extract accurate E values.

We have employed this technique to study several $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds, and we report and discuss our results here. We also had to determine two more crystal structures in order to have both magnetic and structural data for each of two molecules, namely, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeCN})_2 \cdot 2\text{MeCN}$.

The results for $\text{Cr}_2(\text{O}_2\text{CNET}_2)_4(\text{NET}_2\text{H})_2$ provide a beautiful example of how the singlet–triplet gap can be changed appreciably by changing the electronic properties of the bridging ligands while the Cr–Cr distance is but little altered. For this compound the Cr–Cr distance, 2.384 (2) Å, is very similar to those for the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds with $\text{L} = \text{MeOH}$, H_2O , py , or MeCN , and yet the S–T gap is much smaller, viz., ca. 600 cm^{-1} .

Experimental Section

All syntheses, manipulations, and NMR studies were carried out under an inert atmosphere by using standard Schlenk techniques or a glovebox.

Syntheses. The compounds $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$,⁶ $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{py})_2$,⁷ and $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$ ⁴ were prepared by reported methods. Anhydrous $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ was obtained by heating $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot (\text{H}_2\text{O})_2$ at 110°C in vacuo for 24 h. Crystals of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$ (1) and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeCN})_2 \cdot 2\text{MeCN}$ (2) were grown from saturated solutions of anhydrous $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ in methanol and acetonitrile, respectively, at -20°C . The compound $\text{Cr}_2(\text{O}_2\text{CNET}_2)_4(\text{NET}_2\text{H})_2$ was kindly supplied by Prof. F. Calderazzo, who will report a new method for its preparation.⁸

NMR Method. ^1H NMR studies on the acetate compounds were carried out on a Varian XL-200E spectrometer at 200.1 MHz, while ^{19}F NMR studies of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$ were conducted on a Varian XL-400 spectrometer at 376.4 MHz. All variable-temperature spectra were recorded in appropriate solvents within the widest possible temperature range with 10°C intervals and a preacquisition delay of 10 min.

Results

Variable-temperature NMR studies of $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ ($\text{R} = \text{CH}_3$, $\text{L} = \text{MeOH}$, H_2O , py , MeCN ; $\text{R} = \text{CF}_3$, $\text{L} = \text{Et}_2\text{O}$; $\text{R} = \text{NET}_2$, $\text{L} = \text{NET}_2\text{H}$) showed that, in all cases, the chemical shift of the nucleus in question experiences a downfield shift as the temperature increases. It is this temperature dependence of the chemical shifts that allows calculation of the hyperfine coupling constant (A), the diamagnetic chemical shift (δ_{dia}) for the proton

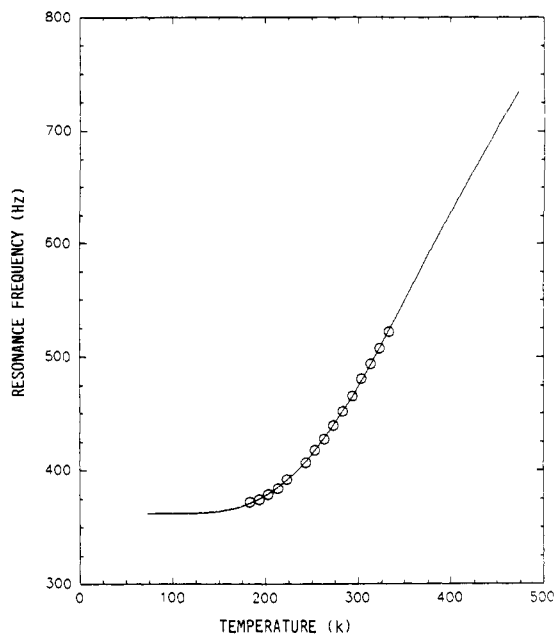


Figure 1. Plot of the acetate proton chemical shift vs absolute temperature for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$. Circles are experimental points, and the solid curve is the theoretical fit. Analogous plots were obtained for all other compounds investigated.

Table I. Calculated Magnetic and Electronic Parameters for $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$

compound	E , cm^{-1}	A , MHz	δ_{dia} , ppm
$\text{R} = \text{Me}$, $\text{L} = \text{MeOH}^a$	1004	0.3363	1.81
$\text{R} = \text{Me}$, $\text{L} = \text{H}_2\text{O}^b$	980	0.3677	1.68
$\text{R} = \text{Me}$, $\text{L} = \text{py}^b$	958	0.3236	1.72
$\text{R} = \text{Me}$, $\text{L} = \text{MeCN}^c$	926	0.3478	1.69
$\text{R} = \text{CF}_3$, $\text{L} = \text{Et}_2\text{O}^d$	462	0.1728	54.60
$\text{R} = \text{NET}_2$, $\text{L} = \text{NHET}_2^e$ CH_3	611	0.0106	2.74
$\text{R} = \text{NET}_2$, $\text{L} = \text{NHET}_2^e$ CH_2	578	0.0388	0.78

^aRecorded in CD_3OD . ^bRecorded in acetone- d_6 . ^cRecorded in CD_3CN . ^dRecorded in Et_2O . ^eRecorded in toluene- d_8 .

(or the fluorine) site, and the S–T energy separations (E) from the equation

$$H_{\text{obs}} = H_{\text{dia}} + \frac{2g\beta H_{0(\text{N})}A}{(\gamma_{(\text{N})}/2\pi)kT}(3 + e^{E/kT})^{-1} \quad (2)$$

where H_{obs} is the frequency of the ^1H or ^{19}F resonance, H_{dia} is the frequency that the same nucleus would have in an equivalent diamagnetic environment, T is the absolute temperature, and the other terms have their usual meanings.

The values of E , H_{dia} , and A were calculated by using a multiple-parameter, nonlinear least-squares procedure to fit the variable-temperature NMR data to eq 2. Figure 1 shows a typical plot of resonance frequency versus temperature, namely, that of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$. Calculated parameters for all compounds investigated are reported in Table I.

Notably, the variation in the chemical shift values for $\text{Cr}_2(\text{O}_2\text{CNET}_2)_4(\text{NET}_2\text{H})_2$ is much smaller than those for the dichromium acetate compounds. This is due to the fact that the protons in the carbamate compound are further removed from the dichromium centers than those in the acetates. This is also manifested in the much smaller electron–nucleus hyperfine coupling constants (A values). A positive “ A ” value for each of the compounds investigated is characteristic of the downfield shift of the signal with temperature. The singlet–triplet separations for dichromium acetate compounds were found to be ca. 900–1000 cm^{-1} , while those for $\text{Cr}_2(\text{O}_2\text{CNET}_2)_4(\text{NET}_2\text{H})_2$ and $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$ are much lower (ca. 600 and 462 cm^{-1} , respectively). The E values for the carbamate compound were calculated from both methyl protons and methylene protons and showed satisfactory agreement.

(3) Bilgrien, C. J.; Drago, R. S.; O’Conner, C. J.; Wong, N. *Inorg. Chem.* **1988**, *27*, 1410.

(4) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.

(5) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915.

(6) Kranz, M.; Witkowska, A. *Inorg. Synth.* **1960**, *6*, 144.

(7) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 328.

(8) Calderazzo, F. Unpublished results.

Table II. Singlet-Triplet Separations and Bond Distances for $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ and $\text{Cu}_2(\text{O}_2\text{CC}_3\text{H}_7)_4$

compound	Cr-Cr, Å	Cr-L, Å	E , cm^{-1}
R = Me, L = MeOH ^{9a}	2.329 (2)	2.264 (7)	1004
R = Me, L = H ₂ O ⁶	2.362 (1)	2.272 (3)	980
R = Me, L = py ⁷	2.369 (2)	2.335 (5)	958
R = Me, L = MeCN ^{9b}	2.396 (6)	2.34 (2)	926
R = CF ₃ , L = Et ₂ O ⁴	2.541 (1)	2.244 (3)	462
R = NEt ₂ , L = NHEt ₂ ¹⁵	2.384 (2)	2.452 (8)	595
$\text{Cu}_2(\text{O}_2\text{CC}_3\text{H}_7)_4$ ¹²	2.584 (1)		310

Although high-quality crystals were not available, qualitative crystallographic studies of the compounds $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$ (1) and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{MeCN})_2 \cdot 2\text{MeCN}$ (2) revealed Cr-Cr distances of 2.329 (2) and 2.396 (6) Å, respectively,⁹ and Cr-L distances of 2.264 (7) and 2.34 (2) Å, respectively.

Discussion

The experimental data establish that the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ molecules have a ground state with no unpaired electrons and a low-lying spin-triplet state. They also show that the energy required for thermal excitation to this triplet state varies inversely with the Cr-Cr distance, as well as with the nature of R.

On the basis of these facts, as well as other knowledge about such compounds, what can be said, and with how much certainty, as to the nature of the ground state and the nature of the triplet state? By the word "nature" we mean, essentially, what electron configuration the state arises from. The magnetic data, taken in isolation, would not allow us to rule out the possibility that there is no Cr-Cr bond in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, but only a strong antiferromagnetic coupling between two Cr^{2+} cores each with $S = 2$. This would, as is well-known,¹⁰ lead to a ladder of states characterized by total spin with the following quantum numbers and relative energies (in parentheses):

$$0(0), 1(E), 2(3E), 3(6E), 4(10E)$$

With E in the range 500–1000 cm^{-1} , and a temperature cutoff of ca. 300 K in the magnetic data, only the first excited state (with total spin of 1) has a detectable effect on the measurable magnetic behavior, and it is therefore impossible to tell whether the rest of the ladder exists or not. Although this may not have been obvious at the time of Furlani's publication, on the basis of the contemporary wealth of spectroscopic and theoretical information,¹ the idea that no Cr-Cr bonds exist and only antiferromagnetic dipolar couplings need be considered is today obviously inadmissible.

Calculations by Hartree-Fock, SCF- $X\alpha$, or similarly rigorous methods show that the ground states of the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ molecules should be based on a $\sigma^2\pi^4\delta^2$ configuration, although considerable configuration interaction renders the actual state of affairs more complex. However, neither theory nor any spectroscopic data speak directly to the question of what configuration might be chiefly responsible for the lowest-lying triplet state. It has been suggested³ that because of weakening of the Cr-Cr bonding, a triplet state derived from the $\sigma^2\pi^4\delta\sigma^*$ configuration might deserve consideration. While this possibility cannot be firmly excluded, neither does it have any explicit support. Two appealing possibilities are triplet states derived from other configurations $\sigma^2\pi^4\delta\delta^*$ ($^3A_{2u}$) or $\sigma^2\pi^4\delta\pi^*$ (3E_g). There are no theoretical results capable of distinguishing between these with certainty, but it seems likely that the $^3A_{2u}$ state would be lower,

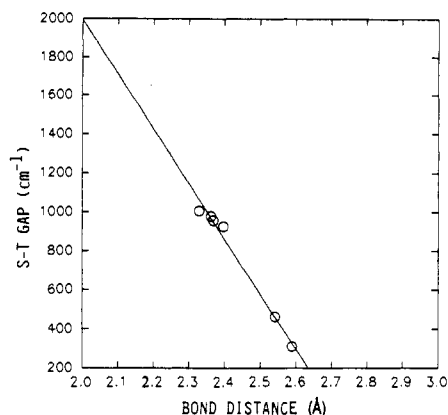
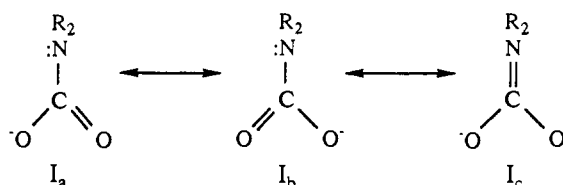


Figure 2. Plot of S-T gap vs Cr-Cr distance for the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds. The last point is for copper(II) *n*-butyrate.

as it certainly is in the $\text{Mo}_2(\text{O}_2\text{CR})_4$ analogs and related $\text{Mo}_2\text{X}_8\text{L}_4$, $\text{Mo}_2\text{X}_8^{4-}$, and $\text{Re}_2\text{X}_8^{2-}$ species. This assumption is not inconsistent with the assignment¹¹ of a band at 21 000 cm^{-1} in the spectrum of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ to the $^1A_{1g} \rightarrow ^1E_g$ ($\delta \rightarrow \pi^*$) transition. It is not likely that the corresponding $^1A_{1g} \rightarrow ^3E_g$ transition would be as low as a few hundred wavenumbers, if this assignment is correct.

In Figure 2 the S-T gaps are plotted versus the Cr-Cr distance for the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds (R = CH₃, CF₃), while the corresponding data are reported in Table II. Although the relationship is approximately linear over the Cr-Cr range covered, it is not expected that this would continue at shorter distances. Instead, a marked upturn would probably occur. It is interesting that the corresponding data for $\text{Cu}_2(\text{O}_2\text{CC}_3\text{H}_7)_4$ ¹² fit on the same line. This is consistent with the views of Figgis and Martin¹³ and Hansen and Ballhausen¹⁴ that the S-T gap in the copper acetate dimers is based on a pair of states which are derived from δ^2 and $\delta\delta^*$ configurations, all other electrons being paired in both.

On the other hand, the compound $\text{Cr}_2(\text{O}_2\text{CNET}_2)_4(\text{NET}_2\text{H})_2$ does not fit on the line defined by the other chromium compounds. Instead, for the Cr-Cr distance found, the S-T gap is much too small. This can be accounted for in a way that is consistent with the idea that the S-T gap is between $^1A_{1g}$ ($\sigma^2\pi^4\delta^2$) and $^3A_{2u}$ ($\sigma^2\pi^4\delta\delta^*$) states. The carbamate ligand has a more electron-rich π system than does the carboxyl ligand because of the contribution of I_c , which has no counterpart in a resonance hybrid description



of a carboxyl anion. Thus, on the δ and δ^* orbitals of the Cr_2^{4+} core, the R_2NCO_2^- ligand would be expected to exert an influence different from that of a RCO_2^- ligand. To determine the net effect of this difference on the δ and δ^* orbitals, and thus on the S-T gap, a quantitative calculation is necessary.

Such a calculation has been carried out by the SCF- $X\alpha$ -SW method for two model molecules, namely, $\text{Cr}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CNH}_2)_4$, where structure parameters from the literature were employed.¹⁵ The calculations employed essentially the same assumptions and procedures as those previously described.¹⁶ The results for the $\text{Cr}_2(\text{O}_2\text{CH})_4$ model were essentially as previously

(9) (a) Compound 1, $\text{Cr}_2\text{O}_{10}\text{C}_{10}\text{H}_{20}$ ($M = 404.26$), crystallizes in space group $P2_1/n$ (No. 14); $a = 8.171$ (2) Å, $b = 7.439$ (1) Å, $c = 13.367$ (3) Å, $\beta = 92.681$ (2)°, $V = 811.6$ (3) Å³, $Z = 2$, $D_{\text{calc}} = 1.655$ g·cm⁻³; $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, AFC5R, $4^\circ < 2\theta < 120^\circ$, $\mu = 233.357$ cm⁻¹, $T = 293$ K, $R(F_o) = 0.062$, $R_w(F_o) = 0.106$ for 910 reflections having $I > 3\sigma(I)$. (b) Compound 2, $\text{Cr}_2\text{O}_8\text{N}_4\text{C}_{16}\text{H}_{24}$ ($M = 504.38$), crystallizes in space group $P2_1/n$ (No. 14); $a = 10.722$ (7) Å, $b = 10.184$ (11) Å, $c = 10.957$ (12) Å, $\beta = 102.07$ (9)°, $V = 1170$ (3) Å³, $Z = 2$, $D_{\text{calc}} = 1.432$ g·cm⁻³; $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, Enraf-Nonius CAD4, $4^\circ < 2\theta < 45^\circ$, $\mu = 9.496$ cm⁻¹, $T = 223$ K, $R(F_o) = 0.103$, $R_w(F_o) = 0.128$ for 618 reflections having $I > 3\sigma(I)$.

(10) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: Oxford, U.K., 1932.

(11) (a) Kok, R. A.; Hall, M. B. *Inorg. Chem.* **1985**, *24*, 1542. (b) Davy, R. B.; Hall, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1268. Earlier work is cited in these two papers.

(12) Campbell, G. C.; Haw, J. F. *Inorg. Chem.* **1988**, *27*, 3706.

(13) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837.

(14) Hansen, A. E.; Ballhausen, C. J. *Trans. Faraday Soc.* **1965**, *16*, 631.

(15) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1978**, *17*, 3536.

(16) Cotton, F. A.; Stanley, G. G. *Inorg. Chem.* **1977**, *16*, 2688.

reported, whereas for $\text{Cr}_2(\text{O}_2\text{CNH}_2)_4$ it was found that while all other MO energies decreased slightly, relative to those in $\text{Cr}_2(\text{O}_2\text{CH})_4$, the energy of the δ orbital rose. The net effect was that the $\delta-\delta^*$ orbital gap decreased from ca. 0.6 eV in $\text{Cr}_2(\text{O}_2\text{CH})_4$ to ca. 0.1 eV in $\text{Cr}_2(\text{O}_2\text{CNH}_2)_4$. While we do not propose to make a quantitative comparison to the experimental S-T data, it is clear that the calculated effect is qualitatively correct and is of about the right magnitude.

Conclusion

While $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds can be (and presumably usually are) contaminated by paramagnetic impurities (most likely Cr(III) species arising by oxidative decomposition), they also have

inherent paramagnetism owing to the existence of a low-lying triplet state. The S-T gap is an inverse function of the Cr-Cr distance but also can be markedly affected by changing the nature of the ligands, e.g., from RCO_2^- to R_2NCO_2^- . A good, but not conclusive, case may be made that the two states (and the principal contributing configurations) that define the S-T gap are $^1\text{A}_{1g}$ ($\sigma^2\pi^4\delta^2$) and $^3\text{A}_{2u}$ ($\sigma^2\pi^4\delta\delta^*$).

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Chris James for advice on fitting the NMR data. We also thank Prof. Carlos A. Murillo for the sample of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$ and Prof. Fausto Calderazzo for that of $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4(\text{NEt}_2\text{H})_2$.

Redox-Active Crown Ethers. Electrochemical and Electron Paramagnetic Resonance Studies on Alkali Metal Complexes of Quinone Crown Ethers

Milagros Delgado,[†] Robert E. Wolf, Jr.,[‡] JudithAnn R. Hartman,[†] Gillian McCafferty,[†] Rahmi Yagbasan,[§] Simon C. Rawle,[†] David J. Watkin,[§] and Stephen R. Cooper^{*†}

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England, Chemical Crystallography Laboratory, University of Oxford, Oxford OX1 3PD, England, and Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received March 20, 1992

Abstract: Structural studies on $[\text{M}(\text{NCS})\cdot(5\text{QC-HQDME})]$ ($\text{M} = \text{Li}, \text{Na}$) as well as free 6QC-HQDME and $[\text{M}(\text{NCS})\cdot(6\text{QC-HQDME})]$ ($\text{M} = \text{Na}, \text{K}$) (where 5QC-HQDME is 15,17-dimethyl-16,18-dimethoxy-3,6,9,12-tetraoxabicyclo-[12.3.1]octadeca(1,14,16)triene, and 6QC-HQDME is 15,17-dimethyl-16,18-dimethoxy-3,6,9,12,15-pentaoxabicyclo-[15.3.1]heneico(1,14,16)triene) show that in all cases the metal ion binds to the anisole oxygen atom in the 1-position. Only in the case of $[\text{K}(\text{NCS})\cdot(6\text{QC-HQDME})]$ do both benzylic O atoms bind to the metal ion; in the other complexes only one of these O atoms interacts with M^+ . In each complex all of the non-benzylic crown O atoms coordinate. These results indicate that the benzylic O atoms contribute suboptimally to complexation. Crystallographic data are as follows: $[\text{Li}(\text{NCS})\cdot(5\text{QC-HQDME})]$, monoclinic, $\text{C}_{19}\text{H}_{28}\text{NO}_6\text{SLi}$, space group $P2_1/n$, $a = 14.103$ (4) Å, $b = 8.493$ (4) Å, $c = 19.128$ (8) Å, $\beta = 108.70$ (9)°, $Z = 4$; $[\text{Na}(\text{NCS})\cdot(5\text{QC-HQDME})]$, monoclinic, $\text{C}_{19}\text{H}_{28}\text{NO}_6\text{SNa}$, space group $P2_1/c$, $a = 10.182$ (4) Å, $b = 8.601$ (1) Å, $c = 25.631$ (3) Å, $\beta = 97.29$ (3)°, $Z = 4$; 6QC-HQDME, orthorhombic, $\text{C}_{20}\text{H}_{32}\text{O}_7$, space group $P2_12_12_1$, $a = 8.195$ (1) Å, $b = 11.541$ (1) Å, $c = 22.449$ (3) Å, $Z = 4$; $[\text{Na}(\text{NCS})\cdot(6\text{QC-HQDME})]\cdot\text{MeCN}$, monoclinic, $\text{C}_{23}\text{H}_{35}\text{N}_2\text{O}_7\text{SNa}$, space group $P2_1/c$, $a = 11.308$ (1) Å, $b = 14.521$ (2) Å, $c = 16.440$ (4) Å, $\beta = 91.56$ (1)°, $Z = 4$; $[\text{K}(\text{NCS})\cdot(6\text{QC-HQDME})]$, monoclinic, $\text{C}_{21}\text{H}_{32}\text{NO}_7\text{SK}$, space group $P2_1/c$, $a = 17.377$ (3) Å, $b = 10.600$ (2) Å, $c = 27.538$ (7) Å, $\beta = 102.41$ (3)°, $Z = 8$. Electrochemical and EPR studies show that redox-active crown ethers incorporating quinone groups successfully couple ion binding by the crown ether to the redox state of the quinone group. Alkali metal ions cause potential shifts that establish-differential redox-induced complexation that qualitatively and quantitatively differs from ion-pairing effects. They also perturb the EPR hyperfine splittings in the semiquinone moieties in a characteristic fashion, as well as in one case giving rise to ^{23}Na superhyperfine splitting.

Introduction

Coupled reactions play an essential role in biology. According to the chemiosmotic hypothesis,¹ energy transduction occurs by coupling discharge of a pH gradient to synthesis of ATP, hydrolysis of which, in turn, drives formation of ion concentration gradients across membranes.² Metabolic pathways drive endothermic reactions by coupling them to other highly exothermic processes.

Outside of biology, coupled reactions most commonly arise from the intrinsic properties of the reactants, and not by design. In a prosaic example, proton displacement upon coordination of a ligand to a metal couples these two reactions; manipulation of pH then influences metal ion binding, and vice versa. In few cases,

however, has one reaction been intentionally coupled to another to which it bears no intrinsic relationship (as opposed to the example above).

Redox-active crown ethers such as I represent one such case of intentional coupling. In suitably designed molecules the proximity of the crown loop to a reducible moiety effectively couples ion binding and redox reactivity, phenomena that would not perturb each other were the two functional groups contained in different molecules.

Quinones offer several advantages as the electroactive component for two reasons. First, they have been thoroughly studied by electrochemical and EPR methods. Second, an obvious but important point, reduction yields the anionic semiquinone; on electrostatic grounds a neutral/anionic couple should yield higher

[†] Inorganic Chemistry Laboratory.

[‡] Harvard University.

[§] Chemical Crystallography Laboratory.

* To whom correspondence should be addressed at the Inorganic Chemistry Laboratory, University of Oxford.

(1) Mitchell, P. *Nature (London)* 1961, 191, 144-148.

(2) Racker, E. *Acc. Chem. Res.* 1979, 12, 338-344.