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Ab Initio Molecular Orbital Calculations of the Ground and Excited States of the Monomeric Linear Dichlorides MCl_2 (Where M = Cr, Co, or Cu)

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Self-consistent field and configuration interaction calculations have been performed in order to describe the ground and excited states of $CrCl_2(g)$, $CoCl_2(g)$, and $CuCl_2(g)$. The calculated transition energies are found to be sensitive to the configurations included but good agreement with experimental data has been obtained in each case. From these ab initio calculations the absorptions at ca. 0.54 and 0.9 μm^{-1} in the electronic spectrum of $CrCl_2(g)$ can be assigned to the transitions ${}^5\Sigma_g^+ \rightarrow {}^5\Pi_g$ and ${}^5\Sigma_g^+ \rightarrow {}^5\Delta_g$, respectively. The ground state of $CoCl_2(g)$ is suggested to be ${}^4\Phi_g$ and the absorptions in the electronic spectrum at 0.52, 1.04, and 1.82 μm^{-1} are assigned to the transitions ${}^4\Phi_g \rightarrow {}^4\Delta_g$, ${}^4\Phi_g \rightarrow {}^4\Sigma_g^-$, and ${}^4\Phi_g \rightarrow {}^4\Pi_g$, respectively. The absorption in the electronic spectrum of $CuCl_2(g)$ at ca. 1.9 μm^{-1} is considered to arise from a Cl 3p to Cu 3d charge-transfer transition, while the structured absorption band occurring between 0.7 and 1.1 μm^{-1} is assigned to the "d–d" transitions ${}^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ and ${}^2\Sigma_g^+ \rightarrow {}^2\Pi_g$.

The electronic spectra of the gaseous transition-metal dichlorides MCl_2 (where M = V, Cr, Fe, Co, Ni, or Cu) have been available for some time[1,2] and these data have been interpreted using various empirical approaches.[1-4] Ab initio molecular orbital (MO) calculations for $CrCl_2$, $CoCl_2$, and $CuCl_2$ have been performed to provide an improved theoretical interpretation of the electronic structure of the ground and excited states of these molecules. No ambiguity arises for the assignment of the spectrum of $CrCl_2$. However, this is not the case for $CoCl_2$ and $CuCl_2$.

Although their symmetry has not been conclusively determined, it is generally believed that the gaseous monomeric 3d transition metal dihalides are linear ($D_{\infty h}$). Thus $MgCl_2$, $CaCl_2$, and $ZnCl_2$ have been shown to be linear by electron diffraction studies of their vapors;[5] a number of transition-metal difluorides and dichlorides do not possess dipole moments;[6] the infrared spectra of matrix-isolated NiF_2 and $NiCl_2$ are consistent with a linear geometry,[7] as are the infrared spectra of gaseous $FeCl_2$, $CoCl_2$, $NiCl_2$, and $CuCl_2$.[8] Therefore a linear geometry was assumed for these calculations.

Computational Details

The ab initio calculations were performed in a basis of Gaussian type functions (GTFs). For Cr and Co, the core orbitals were represented by the minimal basis of Moskowitz et al.,[9] the 4s and 4p orbitals by single GTOs of exponent 0.32, with additional s and p GTOs of exponent 0.08 being added to give variational freedom, and the 3d orbitals by a double-ζ basis of Slater type orbitals (STOs), each STO being fitted by three GTFs. Such a metal basis has previously been found satisfactory in treating the excited states of $CoCl_4^{2-}$.[10] For Cu, the rather larger (8s/4p/2d) basis of Wachter[11] was used, which, however, still gave rather poor d–d excitation energies for $CuCl_4^{2-}$. The chlorine basis used in all calculations was the (6s/4p) set of Dunning.[12]

For each molecule an SCF calculation was performed, corresponding to a convenient d^n metal configuration, and the MOs so produced were used as basis orbitals in configuration interaction (CI) calculations on the other states of interest. Due to the large number of electrons in these molecules, only modest CI calculations were in general performed, the object being to account for the orbital relaxation accompanying electron excitation, rather than to calculate correlation energies. All calculations were performed using the ATMOL system of programs on the CDC 7600 computer of the University of Manchester Regional Computing Centre.

$CrCl_2$. An SCF calculation was performed on the ${}^5\Sigma_g^+$ state of $CrCl_2$ ($\delta_g^2\pi_g^2$). Optimization of the Cr–Cl bond length assuming $D_{\infty h}$ symmetry gave Cr–Cl = 2.35 Å. The CI calculations on $CrCl_2$ were performed at this geometry, using the MOs whose atomic characteristics are shown in Table I. The smallest CI calculation (CI1, Table II) included all d^4 configurations of the correct spin obtained by variable occupancy of the $3\pi_g$, $1\delta_g$, $8\sigma_g$, $9\sigma_g$ MOs; i.e. the bonding MOs arising from the 3d and 4s atomic orbitals. Such a calculation is little more than the virtual orbital approximation.

A second calculation (CI2) included the configurations of CI1, together with the additional single excitations from the filled MOs ($6\sigma_g \ldots 4\pi_u$) to the half-filled MOs ($3\pi_g$ and $1\delta_g$), and from these latter half-filled MOs to the virtual MOs ($8\sigma_g \ldots 12\sigma_g$). A third calculation (CI3) included all the configurations of CI2, plus all single and double excitations to the virtual MOs ($2\delta_g$, $5\pi_g$, and $14\sigma_g$) from the configurations of CI1 and the single excitations from ($6\sigma_g \ldots 4\pi_u$) to ($10\sigma_u$, $11\sigma_g$, $4\pi_g$, and $6\pi_u$) to make a total of 339 bonded functions. These larger calculations therefore allow for orbital relaxation, and the transition energies thus calculated should be near the corresponding SCF values.

$CoCl_2$. The ${}^4F$ and ${}^4P$ free ion terms of a d^7 configuration are split in an environment with $D_{\infty h}$ symmetry into ${}^4\Sigma_g^-$, ${}^4\Phi_g$, ${}^4\Delta_g$, ${}^4\Pi_g$ and ${}^4\Sigma_g^-$, ${}^4\Pi_g$ components, respectively. The 3d-orbital configurations which give rise to these components are listed in Table III in hole notation. A series of CI calculations were carried out to determine the nature of the ground state and the energies of the excited states of $CoCl_2$, using as basis MOs the computed MOs of the ${}^4\Sigma_g^-(F)(\delta_g^4\pi_g^2\sigma_g^1)$ state (Table IV), at the optimized Co–Cl bond length of 2.16 Å. The results of these calculations are summarized in Table V. The first expansion (CI1) included the ten configurations (Table III) arising from the ${}^4F$ and ${}^4P$ free ion terms and gave ${}^4\Phi_g$ as the ground state. In CI2, these ten configurations were taken as reference configurations for double and single excitations from the essentially 3d MOs ($1\delta_g$, $9\sigma_g$, and $3\pi_g$) to the virtual MOs ($2\delta_g$, $5\pi_g$, and $16\sigma_g$), and additional single excitations included in CI2 were those from the filled MOs ($8\sigma_g \ldots 4\pi_u$) to the partially filled MOs ($1\delta_g$, $9\sigma_g$, and $3\pi_g$). CI3 included all of the excitations of CI2 plus the single excitations from the partially filled MOs ($1\delta_g$, $9\sigma_g$, and $3\pi_g$) to the virtual MOs ($10\sigma_g \ldots 10\sigma_u$).

$CuCl_2$. In the case of $CuCl_2$, SCF calculations were performed on the ${}^2\Sigma_g^+$, ${}^2\Pi_g$, and ${}^2\Delta_g$ (d^9) states, the orbital characteristics of ${}^2\Sigma_g^+$ being shown in Table VI. The lowest allowed charge-transfer state was calculated by the SCF method to be a ${}^2\Pi_u$ state, arising from a Cl p to Cu d ($4\pi_u \rightarrow 9\sigma_g$) excitation. A number of CI calculations were performed for each of these four states using the MOs obtained from the SCF calculations. The first CI expansion (CI1) of all four states included single and double excitations from the

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Table I. Orbital Characteristics for the Ground State of $CrCl_2(g)$ $(\ldots 4\pi_u^4 8\pi_g^2 1\delta_g^2)$

		Orbital character, %					
		Chromium			Chlorine		Cr–Cl overlap pop/electron
MO[a]	Energy, au	s	p	d	s	p	
$15\sigma_g$	2.6825			32		68	
$13\sigma_u$	2.4243					98	
$8\pi_u$	2.3952					99	
$6\pi_g$	2.3706					99	
$14\sigma_g$	2.0816	6		60	2	30	
$5\pi_g$	1.8626			99			
$2\delta_g$	1.8183			100			
$13\sigma_g$	1.6438	274		−176	2		
$12\sigma_u$	1.2301		−12		112.5		
$12\sigma_g$	0.9817			−3.5	99	4.5	
$7\pi_u$	0.8351		99				
$11\sigma_u$	0.8248		90		5.5	4	
$6\pi_u$	0.5293		−3			103	
$11\sigma_g$	0.5124	−1		−3	1.5	102	
$10\sigma_u$	0.4955		−6			106	
$4\pi_g$	0.4775					100	
$10\sigma_g$	0.3825	−198		296		2	
$9\sigma_u$	0.2112		116		−16		
$9\sigma_g$	0.1261	43		42	1.5	16	
$5\pi_u$	0.0704		99				
$8\sigma_g$	−0.0293	108		−5	−1	−25	
$1\delta_g$	−0.2406			100			0
$3\pi_g$	−0.2478			98		2	−0.06
$4\pi_u$	−0.4499		4			96	0.05
$2\pi_g$	−0.4570			3		97	0.03
$8\sigma_u$	−0.4661		7		1.5	91.5	0.07
$7\sigma_g$	−0.5141	−3.5		24		76.5	0.16
$7\sigma_u$	−1.0491		3		96		0.07
$6\sigma_g$	−1.0565			4	95		0.07

[a] Numbering includes core levels.

Table II. Calculated Excited States of $CrCl_2(g)$

	State	Transition energy from $^5\Sigma_g^+$, μm^{-1}
CI1	$^5\Sigma_g^+$	0
	$^5\Pi_g$	0.8517
	$^5\Delta_g$	1.2165
CI2	$^5\Sigma_g^+$	0
	$^5\Pi_g$	0.5796
	$^5\Delta_g$	0.9559
CI3	$^5\Sigma_g^+$	0
	$^5\Pi_g$	0.5181
	$^5\Delta_g$	1.0129

Table III. Orbital Description[a] of $D_{\infty h}$ Ligand Field Components for ^4F and ^4P Free Ion Terms

^4F	$^4\Sigma_g^-$	$\pi_{ga}\pi_{gb}\sigma_g$
	$^4\Phi_g$	$2^{-1/2}(\delta_{ga}\pi_{ga}\sigma_g + \delta_{gb}\pi_{gb}\sigma_g)$
		$2^{-1/2}(\delta_{ga}\pi_{gb}\sigma_g - \delta_{gb}\pi_{ga}\sigma_g)$
	$^4\Delta_g$	$\delta_{ga}\pi_{ga}\pi_{gb}$
		$\delta_{gb}\pi_{ga}\pi_{gb}$
	$^4\Pi_g$	$2^{-1/2}(\delta_{ga}\pi_{ga}\sigma_g - \delta_{gb}\pi_{gb}\sigma_g)$
		$2^{-1/2}(\delta_{ga}\pi_{gb}\sigma_g + \delta_{gb}\pi_{ga}\sigma_g)$
^4P	$^4\Sigma_g^-$	$\delta_{ga}\delta_{gb}\sigma_g$
	$^4\Pi_g$	$\delta_{ga}\delta_{gb}\pi_{ga}$
		$\delta_{ga}\delta_{gb}\pi_{gb}$

[a] Hole notation for the d^7 configuration; the subscripts a and b refer to the different orbitals with δ and π symmetry.

valence d orbitals to the virtual d orbitals ($2\delta_g$, $6\pi_g$, $16\sigma_g$, and $17\sigma_g$) and other single excitations to low-lying virtual MOs. These calculations gave transition energies of 0.5978, 0.8230, and 1.2978 μm^{-1}, respectively, for the excitations $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$, $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$, and $^2\Sigma_g^+ \rightarrow {}^2\Pi_u$. The symmetry of the system is such that the number of possible configurations with Σ_g^+ symmetry is considerably greater than those with Π_g, Δ_g, or Π_u symmetry, suggesting that further CI expansions would lower the ground state with respect to the excited states.

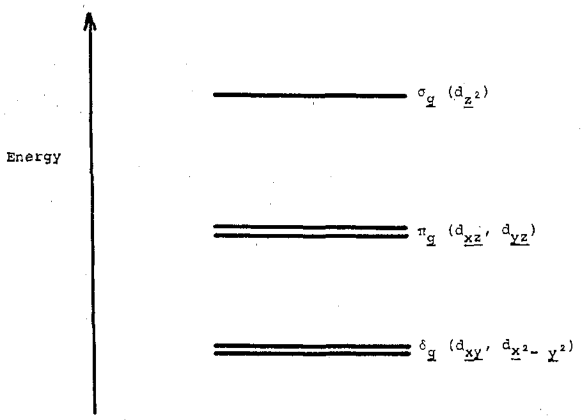

Figure 1. Simple ligand field ordering of d orbitals in $D_{\infty h}$ linear $MCl_2(g)$ molecules.

Further CI calculations for the $^2\Sigma_g^+$ ground state, containing all the configurations of CI1 and including excitations ($7\sigma_g$, $8\sigma_g$) → ($10\sigma_g$, $11\sigma_g$) and $Cl(3p)^2$ → Cu valence orbitals, lowered the ground state by some 0.2253 μm^{-1} and thus led to the calculated transition energies given in Table VII. The computing involved in these calculations was considerable and, for this reason, further such CI calculations were not performed. It seems likely, however, that they would show there to be more correlation energy associated with the $^2\Sigma_g^+$ state than with the other states.

Results and Discussion

$CrCl_2$. Under $D_{\infty h}$ symmetry, simple ligand field arguments for these $MCl_2(g)$ systems suggest the d-orbital energy level sequence shown in Figure 1. For $CrCl_2(g)$, the three possible quintet states are $^5\Sigma_g^+(\delta_g^2\pi_g^2)$, $^5\Pi_g(\delta_g^2\pi_g^1\sigma_g^1)$, and $^5\Delta_g(\delta_g^1\pi_g^2\sigma_g^1)$ and the order of the orbitals given in Figure 1 suggests a $^5\Sigma_g^+$ ground state, with the first and second excited states being $^5\Pi_g$ and $^5\Delta_g$, respectively. The calculations

Table IV. Orbital Characteristics for the ${}^4\Sigma_g^-$(F) State of $CoCl_2$(g) (. . .$4\pi_u^4 1\delta_g^4 9\sigma_g^1 3\pi_g^2$)

		Orbital Character, %					
		Cobalt			Chlorine		Co-Cl overlap pop/electron
MO[a]	Energy, au	s	p	d	s	p	
$16\sigma_g$	2.8500	12		44.5		43.5	
$12\sigma_u$	2.4454					99	
$6\pi_g$	2.3822			10		90	
$8\pi_u$	2.3803					99	
$15\sigma_g$	2.2689	189		−125		35	
$5\pi_g$	2.1349			89		10	
$2\delta_g$	2.0946			100			
$14\sigma_g$	2.0576	128		−52	3	21	
$11\sigma_u$	1.2655		−17		119	−2	
$13\sigma_g$	1.0124	−5			101	4	
$10\sigma_u$	0.7378		86		4	9	
$7\pi_u$	0.7324		97			3	
$12\sigma_g$	0.5650	−205		−302		3	
$6\pi_u$	0.5254		−2			102	
$11\sigma_g$	0.4831	−15		8		106	
$9\sigma_u$	0.4825					100	
$4\pi_g$	0.4699					100	
$8\sigma_u$	0.2227		119		−22	2.5	
$5\pi_u$	0.0820		100				
$10\sigma_g$	0.0568	125		−26	−4	5	
$3\pi_g$	−0.3616			96.5		3	−0.05
$9\sigma_g$	−0.3729	3		90.5		6	−0.09
$4\pi_u$	−0.4727		5			95	0.08
$2\pi_g$	−0.4843			4		96	0.03
$7\sigma_u$	−0.4995		8		2	89.5	0.09
$8\sigma_g$	−0.5704	−4		25	5	73	0.15
$1\delta_g$	−0.7138			100			0
$6\sigma_u$	−1.0793		3.5		95	1	0.05
$7\sigma_g$	−1.0916	0.5		5	92	1.5	0.08

[a] Numbering includes core orbitals.

Table V. Calculated Excited States of $CoCl_2$(g)

	State	Transition energy from ${}^4\Phi_g$, μm^{-1}
CI1	${}^4\Phi_g$	0
	${}^4\Sigma_g^-$	0.1779
	${}^4\Pi_g$	0.2437
	${}^4\Delta_g$	0.2639
	${}^4\Sigma_g^-$	1.5345
	${}^4\Pi_g$	2.2028
CI2	${}^4\Phi_g$	0
	${}^4\Sigma_g^-$	0.1337
	${}^4\Pi_g$	0.2953
	${}^4\Delta_g$	0.5784
	${}^4\Sigma_g^-$	1.3984
	${}^4\Pi_g$	2.3755
CI3	${}^4\Phi_g$	0
	${}^4\Sigma_g^-$	0.1345
	${}^4\Pi_g$	0.2893
	${}^4\Delta_g$	0.5796
	${}^4\Sigma_g^-$	1.3976
	${}^4\Pi_g$	2.2954

performed for this molecule (Tables I and II) confirm this ordering. The data presented in Table I show clearly that the half-filled MOs of the ${}^5\Sigma_g^+$ ground state, $3\pi_g$ and $1\delta_g$, are predominantly (98 and 100%) metal in character, with the former being slightly Cr–Cl antibonding. The other valence MOs are predominantly chlorine in character, although $7\sigma_g$ has a considerable metal component and provides the largest bonding contribution to the Cr–Cl bonds. A Mulliken population analysis of the SCF functions for the ${}^5\Sigma_g^+$ state gave a Cr configuration of $3d^{4.6}4p^{0.4}$ and formal charges of $Cr^{1.04+}$ and $Cl^{0.52-}$.

The absorption spectrum of $CrCl_2$(g)[2] between 0.4 and 2.4 μm^{-1} contains two bands centered at 0.54 and 0.90 μm^{-1}. The extinction coefficients of these bands, 10 and 23 L mol^{-1} cm^{-1}, respectively, are consistent with their assignment as Laporte-forbidden d–d transitions. Ligand field arguments have been presented[2] assigning the absorptions at 0.54 and 0.90 μm^{-1} to the excitations ${}^5\Sigma_g^+ \rightarrow {}^5\Pi_g$ and ${}^5\Sigma_g^+ \rightarrow {}^5\Delta_g$, respectively. The very limited CI calculation CI1 produced an ordering of the states (Table II) in agreement with these assignments. This agreement was maintained for the further CI calculations which produced calculated transition energies in good accord with the experimentally determined values. Relatively little change in the calculated transition energies was observed from CI2 to CI3. However, the energies of all three states were significantally lowered ($\sim$0.68 μm^{-1}) by the inclusion of the excitation to the virtual metal d orbitals $2\delta_g$, $5\pi_g$, and $14\sigma_g$.

$CoCl_2$. A Mulliken population analysis of the SCF MOs of the ${}^4\Sigma_g^-(\delta_g^4\pi_g^2\sigma_g^1)$ state of $CoCl_2$ (Table IV) shows that the half-occupied MOs are predominantly (97 and 94%, respectively) metal in character. Both of these MOs are slightly Co–Cl antibonding; the greatest contribution to the Co–Cl bonds comes from the MO $8\sigma_g$. In this ${}^4\Sigma_g^-$ state, the calculated electronic configuration of the Co atom is $3d^{7.4}4s^{0.1}4p^{0.4}$, the formal charges on the atoms being $Co^{1.02+}$ and $Cl^{0.51-}$.

The electronic absorption spectrum[1,2] of $CoCl_2$(g) is dominated by a structured band (ϵ 54 L mol^{-1} cm^{-1}) with an absorption maximum at ca. 1.43 μm^{-1}. Weaker features are apparent at ca. 2.1(ϵ $\sim$8), 1.82 (sh, ϵ $\sim$13), and 1.04 μm^{-1} (ϵ $\sim$4), and there is a broad absorption tailing into the infrared with a shoulder suggested at ca. 0.54 μm^{-1} (ϵ $\sim$5) and an absorption maximum[1] at ca 0.4 μm^{-1} (ϵ $\sim$7). Assignments of this spectrum based on crystal field arguments have been presented by Hougen et al.[1] and DeKock and Gruen.[2] The former calculated the ground state to be ${}^4\Sigma_g^-$(F) and attributed the absorption at ca. 0.4, 1.04, and 1.43 μm^{-1} to the excitations ${}^4\Sigma_g^-(F) \rightarrow {}^4\Pi_g(F)$, ${}^4\Delta_g$, and ${}^4\Sigma_g^-$(P), respectively. DeKock and Gruen proposed a ${}^4\Phi_g$ ground state and assigned the absorptions observed at ca. 0.4, 1.43 and 1.82 μm^{-1} to the excitations ${}^4\Phi_g \rightarrow {}^4\Delta_g$, ${}^4\Sigma_g^-$(P), and ${}^4\Pi_g$(P), respectively, further

Table VI. Orbital Characteristics for the $^2\Sigma_g^+$ State of $CuCl_2(g)$ $(\ldots 9\sigma_g^1 7\sigma_u^2 4\pi_u^4 3\pi_g^4)$

		Orbital character, %					
		Copper			Chlorine		
MO[a]	Energy, au	s	p	d	s	p	Cu–Cl overlap pop/electron
$17\sigma_g$	4.1946	237		−139		1.6	
$16\sigma_g$	4.0514	63		33		3	
$6\pi_g$	3.6464			99.7			
$2\delta_g$	3.6346			100			
$10\sigma_u$	2.3586					99	
$5\pi_g$	2.3572					99	
$15\sigma_g$	2.3507	−1.5		7	1	93.5	
$6\pi_u$	2.3359					99.9	
$14\sigma_g$	1.0076	−6			102	3	
$9\sigma_u$	0.7757				99		
$13\sigma_g$	0.7403	−116		210		6	
$8\sigma_u$	0.5007					99.9	
$12\sigma_g$	0.4903	−4.5		2.4	2	100	
$4\pi_g$	0.4698					100	
$5\pi_u$	0.4284					99.9	
$11\pi_g$	0.1383	122		−28.5		6	
$10\sigma_g$	0.0015	89		4.5	−4	10.5	
$3\pi_g$	−0.4598			0.5		99.5	−0.012
$4\pi_u$	−0.4675					99.9	−0.001
$7\sigma_u$	−0.4728				2	98	−0.012
$9\sigma_g$	−0.4878	1.5		91		7	−0.034
$8\sigma_g$	−0.5895	9		18.5	7	65	0.103
$1\delta_g$	−0.9297			100			0
$2\pi_g$	−0.9748			99.5		0.5	0.004
$6\sigma_u$	−1.0735				98.5	1.5	0.004
$7\sigma_g$	−1.0898	2		4	92	2	0.081

[a] Numbering includes core molecular orbitals.

Table VII. Calculated Excited States of $CuCl_2(g)$

State	Transition energy from $^2\Sigma_g^+$, μm^{-1}	State	Transition energy from $^2\Sigma_g^+$, μm^{-1}
$^2\Sigma_g^+$	0	$^2\Delta_g$	1.0482
$^2\Pi_g$	0.8230	$^2\Pi_u$	1.5230

noting that the low-intensity absorption in the 0.9–1.1-μm^{-1} region may be identified with transitions to a component of the ^2G state. Angular overlap considerations for $CoCl_2(g)$ were presented by Smith[3] who also favored a $^4\Phi_g$ ground state and assigned the absorptions at ca. 1.04 and 1.82 μm^{-1} to the transitions $^4\Phi_g \rightarrow {}^4\Sigma_g^-(P)$ and $^4\Pi_g(P)$, respectively. The major spectral feature observed[1,2] for $CoCl_2(g)$ was considered[3] to be due to an impurity band arising from a trace of a tetrahedral species. Lever and Hollebone[4] expressed the experimental transition energies of $CoCl_2(g)$ in terms of the crystal field Dq and Ds and the angular overlap e_σ and e_π parameters. These latter authors suggested a $^4\Sigma_g^-(F)$ ground state, with the transitions $^4\Sigma_g^-(F) \rightarrow {}^4\Pi_g(F)$, $^4\Sigma_g^-(P)$, $^4\Delta_g$, and $^4\Pi_g(P)$ being responsible for the absorption at ca. 0.4, 1.04, 1.42, and 2.1 μm^{-1}, respectively.

The CI calculations performed for $CoCl_2(g)$ (Table V) suggest that the electronic ground state is $^4\Phi_g$; however, the $^4\Sigma_g^-$ state is perhaps too close in energy to permit a definitive statement in this respect. The energies of all the states are lowered significantly by the inclusion of the additional excitations from CI1 to CI3, most of the energy lowering arising from the excitations to the virtual metal d orbitals $2\delta_g$ and $5\pi_g$ and the virtual metal–ligand orbital $16\sigma_g$. The calculated transition energies do not immediately suggest an assignment of the spectral data for $CoCl_2(g)$ and a comparison with the results obtained[10] for an ab initio calculation for $CoCl_4^{2-}$, where no ambiguity of assignment exists, is relevant. In the case of $CoCl_4^{2-}$, the observed transition energies were well reproduced for the electronic promotions contained within the levels derived from the ^4F free ion term but were significantly overestimated for the $^4A_2(F) \rightarrow {}^4T_1(P)$ excitation. Thus the values obtained for $^4\Phi_g \rightarrow {}^4\Sigma_g^-$, $^4\Pi_g$, and $^4\Delta_g$ of 0.13, 0.29, and 0.58 μm^{-1}, respectively, could be expected to be reliable estimates for the corresponding transition energies, whereas the values of 1.40 and 2.30 μm^{-1} are anticipated to be substantially in excess of the $^4\Phi_g \rightarrow {}^4\Sigma_g^-(P)$, $^4\Pi_g(P)$ transition energies, respectively. These views are reinforced by ligand field considerations, using a_2 $(=ze^2\bar{r}^2/a^3)$, a_4 $(=ze^2\bar{r}^4/a^5)$, and B values estimated from those established for related systems. The results of the ab initio calculations for $CoCl_4^{2-}$ [10] and $CoCl_2(g)$ afford a similar charge distribution over the Co–Cl separations, and, therefore, it does not seem unreasonable to use the a_4 and B values appropriate to the former, ca. 0.42 and 0.076 μm^{-1} respectively, for $CoCl_2(g)$. The assignment of the spectrum for $CrCl_2(g)$ leads[2] to unambiguous values for a_2 and a_4 for this system and thus a_2 for $CoCl_2(g)$ may be estimated as ca. 0.7 μm^{-1}, given the value of 4.2 above and the a_2/a_4 ratio of 1.67 obtained from $CrCl_2(g)$. Solution of the strong-field matrix for these values of the ligand field parameters yields estimates for the $^4\Phi_g \rightarrow {}^4\Sigma_g^-$, $^4\Pi_g$, $^4\Delta_g$, $^4\Sigma_g^-(P)$, and $^4\Pi_g(P)$ transitions of 0.1, 0.23, 0.6, 0.99, and 1.90 μm^{-1}, respectively. Thus we favor the assignment of the electronic spectrum of $CoCl_2(g)$ as proposed by Smith[3] with features at ca. 0.40, 0.54, 1.04, and 1.82 μm^{-1} being attributed to the $^4\Phi_g \rightarrow {}^4\Pi_g$, $^4\Delta_g$, $^4\Sigma_g^-(P)$, and $^4\Pi_g(P)$ transitions, respectively. The dominant feature of the spectrum at ca. 1.43 μm^{-1} cannot be interpreted in terms of any quartet–quartet transition using either the results of the ab initio calculations or a simple ligand field approach. In view of the confusion surrounding the interpretation of the $CoCl_2(g)$ spectrum, a redetermination of these experimental data would be welcome.

$CuCl_2$. The electronic absorption spectrum[2] of $CuCl_2(g)$ is characterized by two absorptions: a low-energy band with a maximum at 0.9 μm^{-1} and a higher energy band with a maximum at 1.9 μm^{-1}. The three lowest states of $CuCl_2(g)$ are $^2\Sigma_g^+$, $^2\Delta_g$, and $^2\Pi_g$ arising from a ^2D free ion term, and the d-orbital configurations which give rise to these states are $\delta_g^4\pi_g^4\sigma_g^1$, $\delta_g^3\pi_g^4\sigma_g^2$, and $\delta_g^4\pi_g^3\sigma_g^2$, respectively. Two different assignments have been made of the $CuCl_2(g)$ spectrum. Hougen, Leroi, and James[1] proposed that both bands are due to d–d transitions and they assigned the lower energy band to the $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition and the higher energy absorption to the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition. This assignment was later supported by Smith.[3] However, DeKock and Gruen,[2] and subsequently Lever and Hollebone,[4] proposed that the higher energy band is due to a charge-transfer transition, as is suggested by its high intensity (ϵ 3200 L mol^{-1} cm^{-1}), and that the absorption at 0.9 μm^{-1} be assigned to the transition $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$. Using ligand field arguments, the transition $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ would then lie below 0.5 μm^{-1} where it would not be observed. In each of the $3d^9$ states of $CuCl_2$ the valence Cu d orbitals are lower in energy than the predominantly Cl MOs $7\sigma_u$, $4\pi_u$, and $3\pi_g$, with the largest contribution to the bonding in the $^2\Sigma_g^+$ state from the $8\sigma_g$ orbital with approximately 28% metal character (Table VI). The calculated configurations of the copper atom obtained from a Mulliken population analysis of the SCF wave functions of each state are $3d^94s^{0.5}$.

Our proposed assignment of the electronic spectrum of $CuCl_2$(g) using the admittedly rather unsatisfactory results of Table VII is that the band at 1.9 μm^{-1} is due to the excitation $^2\Sigma_g^+ \rightarrow {}^2\Pi_u$ and that the transition energy for $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ occurs in the region 0.7–1.1 μm^{-1}. The $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition may also occur within this latter spectral region which is highly structured[2] and therefore may derive from more than one electronic excitation.

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Insensitivity of the Molybdenum-to-Molybdenum Quadruple Bond in the Dimolybdenum Tetracarboxylates to Axial Coordination and Changes in Inductive Effects

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Several x-ray crytallographic studies have been conducted to determine the response of the Mo–Mo quadruple bond, as that response is evidenced in the bond length, to (a) the presence or absence of axial ligands and (b) changes in the inductive strength of the R group in compounds of the general formula $Mo_2(O_2CR)_4L_2$. The new structures reported here are those of **1**, $Mo_2(O_2CC_6H_5)_4$, and **2**, $Mo_2(O_2CCMe_3)_4$. They are compared with a number of other previously reported structures. Crystal data and some results for **1**: space group $P2_1/c$ with unit cell dimensions a = 5.676 (1) Å, b = 10.339 (2) Å, c = 21.964 (3) Å, β = 94.38 (1)°, V = 1285.3 (3) Å^3, and Z = 2. The $Mo_2(O_2CPh)_4$ molecule has crystallographic C_i symmetry and virtual symmetry which deviates only slightly from D_{4h}. The Mo–Mo distance is 2.096 (1) Å and the mean Mo–O distance is 2.11 (1) Å. The closest intermolecular Mo–O contact is 2.876 (2) Å with an Mo—Mo—O angle of 115.66 (6) °. The structure was refined to R_1 = 0.030 and R_2 = 0.050 using 1476 reflections having $I > 3\sigma(I)$. Crystal data for compound **2**: space group $P\bar{1}$ with unit cell dimensions a = 11.793 (3) Å, b = 12.154 (4) Å, c = 10.403 (4) Å, α = 90.07 (3)°, β = 104.61 (3)°, γ = 71.33 (2)°, V = 1361.8 (7) Å^3, and Z = 2. The $Mo_2(O_2CCMe_3)_4$ molecule has a Mo–Mo distance of 2.088 (1) Å. The mean intramolecular Mo–O distances lie in the range 2.098 to 2.135 Å and the mean axial intermolecular contacts are 2.870 (5) and 2.926 (5) Å. The structure was refined to R_1 = 0.060 and R_2 = 0.085 using 2916 reflections having $I > 3\sigma(I)$.

Introduction

In a compound of the general structure shown in Figure 1 there are three convenient variables: (1) the metal atoms, M and M′; (2) the R group; (3) the axial ligands (which may, of course, be absent). In order to understand the nature of metal–metal quadruple bonds it is useful to study a range of such molecules in which these three variables are altered systematically. In this report we are concerned with systems in which M = M′ = Mo. A forthcoming report will discuss analogous dichromium compounds.

There is already evidence[1] that for Mo_2 systems the M–M bond is very strong, shows little attraction for axial ligands, and is only slightly weakened when axial ligands are present. However, there has been only one simple comparison of an $Mo_2(O_2CR)_4$–$Mo_2(O_2CR)_4L_2$ pair, namely, that in which R = CF_3 and L = pyridine.[2] Since this involves an extremely electron-withdrawing R group, we sought a comparison in which the R group is of intermediate character. For this purpose we have chosen the case where R = C_6H_5 and L = $CH_3OCH_2CH_2OCH_3$. The structure of the $Mo_2(O_2CR)_4L_2$ member of this pair has already been reported[3] and we supply here the data for the corresponding $Mo_2(O_2CR)_4$ compound.

With respect to the effect of the inductive character of R, there are data already available for R = CF_3,[2a] H,[4] and CH_3,[5] that is for R groups ranging from the most strongly electron withdrawing to those of intermediate character. To complete the picture we have examined $Mo_2(O_2CCMe_3)_4$, in which we have the very highly electron-donating *tert*-butyl group, $(CH_3)_3C$.

Experimental Section

The preparations of $Mo_2(O_2CR)_4$, R = CMe_3 and C_6H_5, were done by reaction of $Mo(CO)_6$ with RCO_2H in refluxing *o*-$C_6H_4Cl_2$.[6]

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