DALTON

Bonding in the monochlorides and dichlorides of iron and cobalt

Adam J. Bridgeman

University Chemical Laboratories, Lensfield Road, Cambridge, UK CB2 1EW

The geometries, ground and low-lying excited states of $FeCl_2$, $CoCl_2$, FeCl and CoCl have been studied using local density functional calculations within the linear combination of Gaussian-type orbitals framework. The ground state of $FeCl_2$ is predicted to be $^5\Delta_g$ and that of $CoCl_2$ to be $^4\Sigma_g^-$. These ground states and the predicted order of the excited states require reassignments of the electronic spectra of these molecules. Cellular ligand-field analyses have been performed resulting in excellent agreement with the experimental transition energies. The ground states of FeCl and CoCl are predicted to be $^6\Delta$ and $^3\Sigma^-$ respectively. The dissociation energies of these species have been determined and a comparison of the bonding in these electronically related molecules is presented. These lead to the prediction that the second chloride is bonded more strongly than the first in the dichlorides.

Recent experimental[1–10] and theoretical studies[11–14] on the transition-metal dihalides have shown that the electronic structure of these molecules is not as straightforward as had previously been thought. The ground and low-lying excited states of these molecules arise from the relative occupation of orbitals of mostly metal d-orbital character. The d orbitals in linear molecules are split into three levels and qualitative and quantitative crystal-field arguments and simple molecular orbital considerations suggest that they will have relative energies $d_\sigma > d_\pi > d_\delta$. Previous studies[15–18] of the spectra of $FeCl_2$ and $CoCl_2$ have assumed this order. The ground state of $NiCl_2$ though is predicted[14] to be $^3\Sigma_g^-$ based upon the orbital occupation $(d_\delta)^4(d_\sigma)^2(d_\pi)^2$ due to a reversal in the relative energy of the d_σ and d_π orbitals. This d-orbital ordering was rejected on the basis of angular overlap model (AOM) calculations by Smith[17] and by Lever and Hollebone[18] since it leads to parameter values with $e_\pi > e_\sigma$. This was taken to imply greater π than σ donation in these molecules and was presumed to be unlikely.

An analysis by Bridgeman[14,19] has shown that the ligand field suffered by the d_σ orbital in linear dichloride molecules arises from two sources. The first is the effect of the bonding σ_g function of mostly chlorine sp^n orbital character. This is represented by the positive, antibonding shift $e_\sigma'(Cl)$. The d_σ orbital is also perturbed by the antibonding σ_g function of mostly metal s-orbital character. This acts to stabilize the d_σ orbital and is represented by the negative shift $e_\sigma(\text{void})$ (labelled e_{sd} or σ_{sd} in AOM theory). The observed e_σ parameter is the sum of these two terms, equation (1). The energy shift of the d_σ orbital is

$$e_\sigma = e_\sigma'(\text{Cl}) + e_\sigma(\text{void}) \qquad (1)$$

then given[14] by equation (2). Its magnitude represents the

$$\varepsilon(d_\sigma) = 2e_\sigma'(\text{Cl}) + 2e_\sigma(\text{void}) \qquad (2)$$

relative importance of the two effects. The result $e_\pi > e_\sigma$ does not imply greater π donation. The individual values of the two terms making up e_σ are not obtainable within an AOM or a cellular ligand-field (CLF) modelling of the ligand-field potential in linear molecules.

The geometries adopted by dihalide molecules of the 3d transition metals have also been the subject of controversy. Electron diffraction studies in the gas phase[20,21] and in argon matrices[22] have been interpreted in terms of bent molecules. More recent work by Hargittai and co-workers,[23,24] however, strongly suggests that the molecules are linear. A number of calculations on $FeCl_2$ have previously been reported.[25–27] All predict a $^5\Delta_g$ ground state. No previous non-empirical calculations on $CoCl_2$ have been reported.

The study of the dihalides is assisted in this paper by calculations on the monohalides of iron and cobalt. The electronic spectra of the transition-metal monochlorides are very complicated and in many cases the ground states have not been identified.[28–30] These species are electronically very similar to the dichlorides. The compound FeCl appears to have a $^6\Delta$ ground state[30] and a number of theoretical studies confirm this.[27,31,32] The ground state of CoCl has not been identified and no theoretical studies have been reported; CoF appears to have a $^3\Phi$ ground state.[30] The dissociation energies of the dichlorides and monochlorides are reported together with analyses of the bonding in these species.

Computational Details

All density functional calculations[33–36] were performed here using the DEFT code written by St-Amant[37] in the linear combination of Gaussian-type orbitals (LCGTO) framework. Two types of spin-unrestricted calculations have been completed differing in the treatment of the exchange and correlation interactions. The first set used the Vosko–Wilk–Nusair (VWN) local spin density (LSD) approximation of the correlation part of the exchange-correlation potential.[38] The second set (BP) corrects the LSD expression using the Becke[39] non-local functional for exchange and the Perdew[40] non-local functional for correlation. Stranger and co-workers[41] have investigated the effects of spin polarization and non-local corrections on a variety of $[M_2X_9]^{n-}$ complexes with various spin states. They observe that the introduction of non-local corrections does not necessarily increase the accuracy of the results for the states with high values of *S*.

The Gaussian basis sets (GTOs) and the auxiliary basis sets needed for the Coulomb and exchange potential were optimized specifically for LSD calculations by Godbout *et al.*[42] For iron and cobalt, GTO sets of double-ζ quality were used with the contraction patterns (63321/531*/41+) and (63321/5211*/41+). They contain one d-diffuse and one p-polarization function. For chlorine, double-ζ basis sets with the contraction patterns (6321/521/1*) and (7321/621/1*) and a triple-ζ basis set with the contraction pattern (73311/6111/1*) were used. These sets contain d-polarization functions. All calculations were performed in an all-electron treatment. Vibrational frequencies were calculated by finite differentiation of analytic first derivatives. The symmetric stretch, the bending mode and the antisymmetric stretch are denoted ν_{sym}, ν_δ and ν_{asym} respectively.

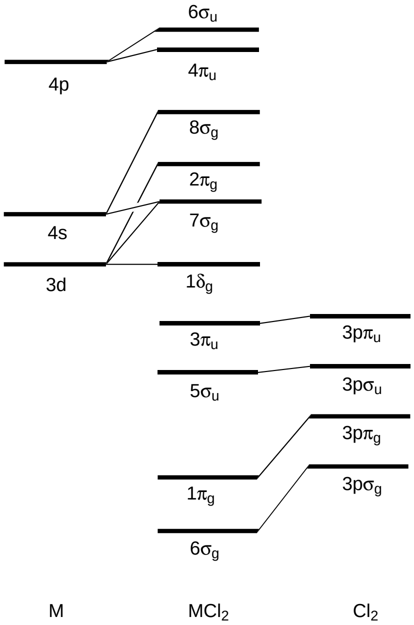

Fig. 1 Qualitative orbital diagram for a linear MCl_2 molecule

Table 1 Calculated and experimentally determined properties of the $^5\Delta_g$ ground state of $FeCl_2$

	Calculated			
	VWN	BP	Experimental	Ref.
Bond length/Å	2.087	2.141	2.128	24
Bond angle/°	180	180	180	23, 24
Vibrational wavenumber/cm^{-1}				
ν_{sym}	315	292	350	48
ν_{asym}	480	442	493	49
ν_δ	85	99	88	50

Table 2 Calculated properties of the low-lying excited states of $FeCl_2$. The molecule is predicted to be linear in all these states

			Vibrational wavenumber/cm^{-1}			
State		Bond length/Å	ν_{sym}	ν_{asym}	ν_δ	Relative energy*/cm^{-1}
$^5\Sigma_g^+$	VWN	2.066	342	525	55	5 450
	BP	2.120	320	498	60	5 200
$^5\Pi_g$	VWN	2.119	319	482	50	6 900
	BP	2.160	310	478	55	6 820
$^1\Sigma_g^+$	VWN	2.020	372	559	56	11 450
	BP	2.050	340	520	42	12 300
$^1\Phi_g$	VWN	2.050	391	573	50	17 970
	BP	2.110	360	555	45	19 300
$^3\Delta_g$	VWN	2.070	315	480	50	9 675
	BP	2.110	295	470	45	9 950

* Compared to the $^5\Delta_g$ ground state.

Dissociation energies were calculated from the energies of the species at the optimized bond lengths.

Metal–chlorine σ- and π-bond orders were calculated according to the prescription suggested by Mayer.[43] The relative degrees of σ- and π-charge transfer, denoted Δσ and Δπ respectively, in each state were determined from the changes in Mulliken populations compared to the fully ionic $M^{2+}2Cl^-$ and M^+Cl^- formulation with the metal ion in the appropriate crystal-field configuration.

The high-spin states for each of the systems can be described with single determinants built from the occupation of one-electron orbitals. The ground states of each molecule are in this class and can therefore be well established by the calculations presented here. For the lower spin states the configurations give rise to several states and a single-determinant approach is less valid. The optimized geometries of the low-spin electron arrangements will necessarily be an average of those of each of these states. It should be stressed that the primary aim of the calculations is to establish the ground states of each system. The discussion of the low-spin states is limited to a brief discussion of the effect of the change in electron configuration on the bonding properties. Ligand-field calculations have a proven record in the reliable calculation of excited states within the ligand-field regime.

The cellular ligand field (CLF) model of Gerloch and Woolley[44–46] has been used successfully for many years to model the ligand-field properties of transition-metal complexes. The CLF calculations were performed on $FeCl_2$ and $CoCl_2$ using the CAMMAG 4 suite of programs.[47] The CLF parameters e_σ and e_π(Cl) were used for the σ and π interactions between the transition metal and chlorine. The analyses also required the 'central' Racah parameters B and C for interelectron repulsion and ζ for spin–orbit coupling.

Results

Fig. 1 shows a qualitative orbital energy diagram for a linear metal dichloride molecule. The ground and low-lying excited states in $FeCl_2$ and $CoCl_2$ arise from the possible arrangements of the six or seven respectively metal-based electrons within the 'd orbitals' labelled $1\delta_g$, $7\sigma_g$ and $2\pi_g$.

(*a*) $FeCl_2$

The DFT calculations predict $FeCl_2$ to be a linear molecule with a $^5\Delta_g$ ground state arising from the configuration $(1\delta_g)^3(7\sigma_g)^1(2\pi_g)^2$. Table 1 lists the calculated and experimentally determined geometry and vibrational frequencies of the ground state obtained using the less contracted iron basis set and the triple-ζ chlorine basis set. Calculations using the more contracted iron set led to a bond length around 1 pm longer. The double-ζ chlorine basis sets led to smaller changes in the Fe–Cl bond length. The analyses and discussion given below are based on the calculations using the less contracted iron set and the triple-ζ chlorine set. The inclusion of non-local corrections in the BP calculations was found to cause a significant increase in the Fe–Cl bond length and considerably better agreement with the experimentally determined value. The agreement between the calculated and experimental vibrational frequencies, however, is found to decrease upon the introduction of non-local corrections. The work of Stranger and co-workers[41] has similarly shown that non-local corrections do not necessarily increase the accuracy of the calculations.

The $^5\Delta_g$ ground state agrees with that favoured by previous workers[15–18,25–27] as it does not depend on the ordering of $7\sigma_g$ and $2\pi_g$. As a direct consequence of the reversal of relative energies of these orbitals, however, the $^5\Pi_g$ $(1\delta_g)^2(7\sigma_g)^1(2\pi_g)^3$ state is predicted to lie at higher energy than $^5\Sigma_g^+$ $(1\delta_g)^2(7\sigma_g)^2$-$(2\pi_g)^2$. The lowest-lying spin-singlet and spin-triplet states are predicted to lie at much higher energy. Table 2 lists the calculated geometries, vibrational frequencies and relative energies of these excited states. All of the states studied are predicted to be linear. The calculated bond orders and charge transfers for the ground and excited states obtained from the VWN calculations are presented in Table 3.

The spectrum[16] of gaseous $FeCl_2$ shows bands at 4600 and 7140 cm^{-1}. These bands have previously been assigned[15–18] to the $^5\Pi_g \longleftarrow {}^5\Delta_g$ and $^5\Sigma_g^+ \longleftarrow {}^5\Delta_g$ transitions respectively. The DFT results suggest a reversal of the assignment of these bands. Table 4 lists the calculated and observed transition energies resulting from this reassignment and the CLF parameter values shown in Table 5. This table also includes CLF par-

Table 3 Bonding in the ground and low-lying excited states of $FeCl_2$

State	$^5\Delta_g$	$^5\Sigma_g^+$	$^5\Pi_g$	$^1\Sigma_g^+$	$^1\Phi_g$	$^3\Delta_g$
Configuration *	$\delta_g{}^3\sigma_g{}^1\pi_g{}^2$	$\delta_g{}^2\sigma_g{}^2\pi_g{}^2$	$\delta_g{}^2\sigma_g{}^1\pi_g{}^3$	$\delta_g{}^4\sigma_g{}^2\pi_g{}^0$	$\delta_g{}^3\sigma_g{}^2\pi_g{}^1$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^2$
Bond order						
total	1.08	1.06	0.99	1.41	1.22	0.95
σ	0.61	0.48	0.60	0.52	0.50	0.65
π	0.47	0.58	0.39	0.89	0.74	0.30
Charge transfer/ electron						
total	1.50	1.59	1.47	1.85	1.68	1.55
σ	0.69	0.63	0.79	0.65	0.62	0.80
π	0.82	0.95	0.67	1.20	1.06	0.75

* Approximate description.

Table 4 Calculated spin orbit level (Ω) and observed transition energies (in cm^{-1}) in the ligand-field spectrum of $FeCl_2$

State	Strong-field configuration *	Ω	Calculated	Observed[16]
$^5\Pi_g$	$\delta_g{}^2\sigma_g{}^1\pi_g{}^3$	1	7346	
		0+	7296	
		0−	7242	
		1	7182	7140
		2	7089	
		3	6980	
$^5\Sigma_g^+$	$\delta_g{}^2\sigma_g{}^2\pi_g{}^2$	2	4730	
		1	4704	4600
		0+	4696	
$^5\Delta_g$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^2$	0+	695	
		0−	695	
		1	518	
		2	343	
		3	170	
		4	0	0

* Approximate description.

Table 5 The CLF and central parameter values (in cm^{-1}) for $FeCl_2$, $[FeCl_4]^{2-}$ and $[FeCl_6]^{4-}$ and for $CoCl_2(g)$, $CoCl_2(s)$ and $[CoCl_4]^{2-}$

Compound	$e_\sigma(Cl)$	$e_\pi(Cl)$	$e_\pi(Cl)/e_\sigma(Cl)$	B	ζ	Ref.
$FeCl_2$	2200	3400	1.55	—	350	*a*
$[FeCl_4]^{2-}$ [b]	4560	1140	0.25	—	—	51
$[FeCl_6]^{4-}$ [c]	3760	940	0.25	—	550	52
$CoCl_2(g)$ [d]	4300	4500	0.96	550	450	*a*
$CoCl_2(s)$ [b]	3350	840	0.25	780	700	53
$[CoCl_4]^{2-}$ [c]	3400	850	0.25	710	700	54

[a] This work. [b] The CLF parameter values were obtained from Δ_{tet} assuming $e_\sigma \approx 4e_\pi$. [c] The CLF parameter values were obtained from Δ_{oct} assuming $e_\sigma \approx 4e_\pi$. [d] $C = 3200$.

Table 6 Calculated and experimentally determined properties of the $^4\Sigma_g^-$ ground state of $CoCl_2$

	Calculated			
	VWN	BP	Experimental	Ref.
Bond length/Å	2.040	2.103	2.090	24
Bond angle/°	180	180	180	24
Vibrational wavenumber/cm^{-1}				
ν_{sym}	338	308	359	48
ν_{asym}	513	445	493	49
ν_δ	86	90	95	50

Table 7 Bonding in the ground and low-lying excited states of $CoCl_2$

State	$^4\Sigma_g^-$	$^4\Delta_g$	$^4\Phi_g$	$^2\Pi_g$
Configuration *	$\delta_g{}^4\sigma_g{}^1\pi_g{}^2$	$\delta_g{}^3\sigma_g{}^0\pi_g{}^2$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^3$	$\delta_g{}^4\sigma_g{}^2\pi_g{}^1$
Bond order				
total	0.94	0.96	0.92	1.10
σ	0.47	0.40	0.54	0.40
π	0.47	0.56	0.83	0.70
Charge transfer/ electron				
total	1.68	1.52	1.51	1.68
σ	0.70	0.54	0.89	0.52
π	0.99	0.98	0.62	1.16

* Approximate description.

Table 8 Calculated properties of the low-lying excited states of $CoCl_2$. The molecule is predicted to be linear in all these states

State		Bond length/Å	Vibrational wavenumber/cm^{-1}			Relative energy */cm^{-1}
			ν_{sym}	ν_{asym}	ν_δ	
$^4\Delta_g$	VWN	2.045	335	499	45	3 200
	BP	2.099	306	447	30	2 500
$^4\Phi_g$	VWN	2.083	333	478	30	4 000
	BP	2.142	302	425	35	3 600
$^2\Pi_g$	VWN	2.026	336	505	35	10 120
	BP	2.056	299	478	40	9 960

* Compared to the $^4\Sigma_g^-$ ground state.

ameter values obtained from analyses of tetrachloro- and hexachloro-ferrate(II) complexes for comparison.

(*b*) $CoCl_2$

The DFT calculations predict $CoCl_2$ to be a linear molecule with a $^4\Sigma_g^-$ ground state resulting from the configuration $(1\delta_g)^4(7\sigma_g)^1(2\pi_g)^2$. The calculated and experimentally determined geometry and vibrational frequencies obtained using the less contracted cobalt basis set and the triple-ζ chlorine basis set are listed in Table 6. The calculated metal–chlorine bond was again found to be more sensitive to the quality of the metal basis set than to that used for chlorine. Similarly, the BP calculations led to better agreement with the experimentally determined bond length but a decrease in the agreement between experimental and calculated vibrational frequencies.

The $^4\Sigma_g^-$ ground state agrees with that predicted by Lever and Hollebone[18] but disagrees with the $^4\Phi_g$ ground state assumed by Hougen *et al.*,[15] DeKock and Gruen[16] and by Smith.[18] All of the states studied are predicted to be linear. The calculated bond orders and charge transfers for the ground and excited states obtained from the VWN calculations are presented in Table 7.

The previous workers however assumed an underlying d-orbital ordering $d_\delta < d_\pi < d_\sigma$. The $^4\Sigma_g^-$ state is a possible ground state whatever the order of d_π and d_σ. The order of the excited states and so the assignment of the electronic spectrum, however, are dependent on this order. Table 8 lists the calculated geometries, vibrational frequencies and relative energies of some of the excited states. The $^4\Delta_g$ state arises from exciting an electron from $1\delta_g$ to $7\sigma_g$. The $^4\Phi_g$ state arises from the $1\delta_g \longrightarrow 2\pi_g$ orbital excitation. The $^4\Delta_g$ state is predicted to lie at slightly lower energy than $^4\Phi_g$, consistent with the d-orbital

Table 9 Calculated spin orbit values (Ω) and observed transition energies (in cm^{-1}) in the ligand-field spectrum of $CoCl_2$

State[a]	Strong-field configuration *	Ω	Calculated	Observed[15,16]
$^4\Pi_g(P)$	$\delta_g{}^2\sigma_g{}^2\pi_g{}^3$	1/2	18 338	
		3/2	18 141	18 200
		1/2	18 028	
		5/2	17 959	
$^2\Pi_g(H)$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^3$	1/2	16 890	
		3/2	16 929	
$^2\Phi_g(G)$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^3$	5/2	16 584	
		7/2	16 021	
$^2\Delta_g(H)$	$\delta_g{}^3\sigma_g{}^2\pi_g{}^2$	3/2	15 745	
		5/2	15 198	
$^2\Gamma_g(G)$	$\delta_g{}^2\sigma_g{}^1\pi_g{}^4$	7/2	15 638	
		9/2	15 144	
$^4\Sigma_g^-(P)$	$\delta_g{}^2\sigma_g{}^1\pi_g{}^4$	1/2	14 644	
		3/2	14 596	14 200
$^2\Pi_g(P)$	$\delta_g{}^4\sigma_g{}^0\pi_g{}^3$	3/2	14 231	
		1/2	13 821	
$^2\Sigma_g^+(P)$	$\delta_g{}^3\sigma_g{}^2\pi_g{}^2$	1/2	13 072	
$^2\Delta_g(G)$	$\delta_g{}^4\sigma_g{}^1\pi_g{}^2$	5/2	12 398	
		1/2	12 300	
$^2\Sigma_g^+(G)$	$\delta_g{}^4\sigma_g{}^1\pi_g{}^2$	1/2	10 995	
$^2\Pi_g(G)$	$\delta_g{}^4\sigma_g{}^2\pi_g{}^1$	3/2	10 476	10 400
		1/2	10 053	
$^4\Pi_g(F)$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^3$	1/2	5 352	5 200 (extending to lower energy)
		1/2	5 277	
		3/2	5 150	
		5/2	4 972	
$^4\Phi_g(F)$	$\delta_g{}^3\sigma_g{}^1\pi_g{}^3$	3/2	3 961	
		5/2	3 590	
		7/2	3 156	
		9/2	2 550	
$^4\Delta_g(F)$	$\delta_g{}^3\sigma_g{}^2\pi_g{}^2$	1/2	3 195	
		3/2	2 800	
		5/2	2 477	
		7/2	2 243	
$^4\Sigma_g^-$**(F)**	$\delta_g{}^4\sigma_g{}^1\pi_g{}^2$	3/2	6	
		1/2	0	0

* Approximate description.

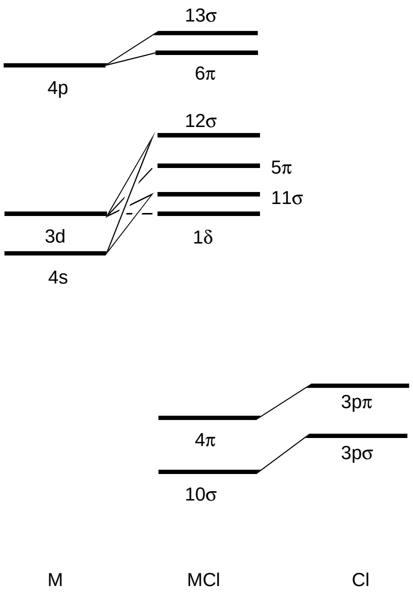

Fig. 2 Qualitative orbital diagram for an MCl molecule

ordering $d_\delta < d_\sigma < d_\pi$ as found for $FeCl_2$ above and for[14,19] $NiCl_2$, $CuCl_2$, $[NiO_2]^{2-}$ and NiO(g). The energy of these two states is reversed in the calculations of Lever and Hollebone[18] with the $^4\Delta_g$ state lying at very high energy. The lowest-lying spin-doublet state is predicted to be $^2\Pi_g$. This state arises from the low-spin configuration $(1\delta_g)^4(7\sigma_g)^2(2\pi_g)^1$ and its energy is consistent with the same underlying d-orbital ordering as discussed above.

The gas-phase spectrum of $CoCl_2$ contains[15,16] an intense band at 14 200 cm^{-1} with weaker bands at low energy, at 10 400 cm^{-1}, and at high energy at 18 200 cm^{-1}. There is also a band stretching into the infrared with a shoulder at 5200 cm^{-1}. Smith[17] showed that the assignment of Hougen *et al.*[15] and of DeKock and Gruen[16] led to *negative* transition energies for $^4\Sigma_g^- \longleftarrow {}^4\Phi_g$ unless a very small nephelauxetic effect is assumed. Smith rejected the possibility of a $^4\Sigma_g^-$ ground state, however, since it led to calculated spin-allowed bands in transparent regions of the spectrum or to ligand-field parameters based on $e_\sigma < e_\pi$. The latter possibility was rejected as unreasonable. The intense band at 14 200 cm^{-1} was thus assigned by Smith as being due to an impurity.

In view of the analyses of $FeCl_2$, $CuCl_2$, $NiCl_2$, $[NiO_2]^{2-}$ and NiO, the parameters e_σ and e_π were allowed to vary freely in the CLF calculations. Attempting to model the observed spectrum with the order of the low-lying excited states predicted by the DFT calculations described above led to $e_\sigma < e_\pi$, as expected. The calculations suggested the following assignments of the observed spectral bands: (*i*) the high-energy band at 18 200 cm^{-1} is assigned as $^4\Pi_g(P) \longleftarrow {}^4\Sigma_g^-$; (*ii*) the band at 14 200 cm^{-1} is assigned as $^4\Sigma_g^-(P) \longleftarrow {}^4\Sigma_g^-$; (*iii*) the weak band at 10 400 cm^{-1} is assigned as the spin-forbidden $^2\Pi_g(G) \longleftarrow {}^4\Sigma_g^-$ transition; and (*iv*) the infrared band is assigned to transitions to the $^4\Pi_g$, $^4\Phi_g$ and $^4\Delta_g$ components of the ^4F term.

Table 9 lists the calculated and observed transition energies resulting from this reassignment and the CLF parameter values shown in Table 5. This table also includes CLF parameter values obtained from analyses of tetrachloro- and hexachlorocobaltate(II) complexes for comparison. These assignments are consistent with the observed spectrum and the DFT results and are markedly different to those suggested by Lever and Hollebone.[18] They also correspond to the assignment B discussed in the appendix of Smith's paper.

(*c*) FeCl and CoCl

Fig. 2 shows a qualitative orbital scheme appropriate to a 3d transition-metal monochloride. The ground and low-lying excited states for FeCl and CoCl arise from the possible arrangements of the seven or eight electrons of the M^+ ion respectively in the metal-based 1δ, 11σ, 5π and 12σ. These arise from both the metal d and s orbitals. This contrasts with the dichlorides where the low-lying, 'ligand-field' states arise from occupation of the orbitals which are mostly metal d orbital in character. The difference arises from the overall weaker bonding in the monochlorides due to the lower, formally +1, charge on the metal and the much smaller energy gap between the d and s orbitals in this oxidation state. The small energy splitting of the {1δ, 11σ, 5π and 12σ} set of metal-based orbitals allows the possibility of two types of high-spin arrangments of the electrons. Two spin states have been investigated for both FeCl and CoCl. The first corresponds to occupation of only the orbitals of mostly metal d orbital in character (1δ, 11σ and 5π) leading to a spin quartet for FeCl and a spin triplet for CoCl. This corresponds to the situation found in higher-valent transition-metal complexes such as $FeCl_2$ and $CoCl_2$. The second corresponds to occupation of the orbitals of mostly metal d- and s-orbital character (1δ, 11σ, 5π and 12σ) allowing a higher spin multiplicity. This leads to a spin sextet for FeCl and a spin quintet for CoCl.

Table 10 lists the calculated properties of the lowest-energy states for each of these spin arrangements obtained using the less contracted metal basis sets and the triple-ζ chlorine basis set. The ground state of FeCl is predicted to be $^6\Delta$ in agreement with previous studies.[27,30,31] The ground state of CoCl is predicted to be $^3\Sigma^-$, although the $^3\Phi$ state is calculated to be very near in energy. Table 11 lists the calculated bond orders and charge transfers in the lowest-energy states of these systems.

Discussion

(*a*) Dichlorides

The ground states of $FeCl_2$ and $CoCl_2$ are predicted to be linear. This is consistent with the electron diffraction studies of Hargittai and co-workers[23,24] which include the effect of shrinkage due to the large amplitude of the soft bending vibrational mode of these molecules. The calculated charge transfers and bond orders are consistent with σ and π bonding roles enhanced compared to those in complexes with higher co-ordination numbers. The σ bonding is calculated to be marginally more important than the π interaction. The order of the excited states and the assignment of the spectral bands however is only consistent with CLF parameter values with $e_\sigma < e_\pi$ and an underlying d-orbital ordering $d_\delta < d_\sigma < d_\pi$. The relative energy of d_σ and d_π is reversed with respect to that predicted by crystal-field calculations or by simple molecular orbital arguments.[55]

The d orbitals in complexes with π-donor ligands become antibonding functions as a consequence of the interaction with the valence orbitals of the ligands. In linear MCl_2 molecules only the d_σ and d_π orbitals can interact with ligand functions. There are no low-lying ligand-group orbitals of δ symmetry. The 1δ orbitals of the molecules are calculated to be completely metal d orbital in character and to have no bonding or antibonding role. The electronic configurations in the ground states of $FeCl_2$ and $CoCl_2$ differ only in the occupation of the 1δ orbitals, $(1\delta)^3$ and $(1\delta)^4$ respectively. The bonding in these molecules is thus rather similar, as revealed by the calculated bond orders shown in Tables 3 and 7.

Table 10 Calculated properties of the low-lying states of FeCl and CoCl. The experimentally determined[29] properties are listed for comparison

	State		Bond length/Å	Vibrational wavenumber/ cm^{-1}	Relative energy*/ cm^{-1}
FeCl	Experimental		2.088	402	—
	$^6\Delta$	VWN	2.135	382	0
		BP	2.190	344	0
	$^4\Delta$	VWN	2.041	319	1 770
		BP	2.098	310	1 531
CoCl	Experimental		2.093	420	—
	$^5\Sigma^-$	VWN	2.123	372	12 500
		BP	2.176	347	11 500
	$^3\Sigma^-$	VWN	2.024	421	0
		BP	2.083	376	0
	$^3\Phi$	VWN	2.035	350	1 350
		BP	2.060	344	1 120

* Compared to the ground state.

The $7\sigma_g$ orbital in these molecules is dominated in character by the metal d_σ orbital. As outlined above and discussed in detail in refs. 14 and 19, this orbital suffers two perturbations in MCl_2 molecules. The interaction with the ligand-dominated $6\sigma_g$ function causes an antibonding shift. This represents the classical repulsion in crystal-field theory or the dominant σ interaction in simple molecular orbital treatments. The orbital, however, can also interact with the metal 4s-dominated $8\sigma_g$ orbital. As the latter function lies at higher energy than the d orbitals this causes a stabilization of d_σ. The $7\sigma_g$ orbital has substantial amounts of metal 4s character. It is calculated to be approximately 60% d_σ and 20% 4s in both $FeCl_2$ and $CoCl_2$.

The result of the two opposing energy shifts is a rather small e_σ parameter for both molecules and that the $7\sigma_g$ orbital is not particularly antibonding in nature. In valence-bond language, the repulsive interaction between the chlorine lone pairs and the electron(s) in the d_σ orbital can be reduced by sd hybridization. The d_σ electron(s) can then be placed in a cyclindrically symmetric sd hybrid perpendicular to the molecular axis. This hybridization is depicted in Fig. 3. The bonding in the $^5\Sigma_g^+$ and $^4\Delta_g$ excited states of $FeCl_2$ and $CoCl_2$ respectively, corresponding to excitation of an electron from $1\delta_g$ to $7\sigma_g$ in each case, is not substantially different from that in the ground states. In both systems the excitation from $1\delta_g$ to $7\sigma_g$ causes only a small decrease in the σ bonding.

The metal d_π orbitals suffer only an antibonding shift due to the interaction with the ligand π orbitals. The result for $FeCl_2$ and $CoCl_2$ is that the $2\pi_g$ lies above the $7\sigma_g$ in energy corresponding to the d-orbital sequence $d_\delta < d_\sigma < d_\pi$. The DFT results indicate substantial π bonding in these molecules and this results in large e_π parameters compared to the tetrachloro- and hexachloro-metallate(II) systems, as shown in Table 5. Excitation of an electron from the $1\delta_g$ or $7\sigma_g$ to the $2\pi_g$ orbital causes a significant weakening of the bonding as shown, for example, for the $^5\Sigma_g$ and $^4\Phi_g$ excited states of $FeCl_2$ and $CoCl_2$ respectively. The strongest bonding is thus shown in the lowest-lying low-spin states for both systems. The $^1\Sigma_g^+$ state of $FeCl_2$ has no electrons in the strongly antibonding $2\pi_g$ orbital and has an M–Cl bond order approximately 30% higher than that in the ground state. The $^2\Pi_g$ state of $CoCl_2$ has a single electron in the

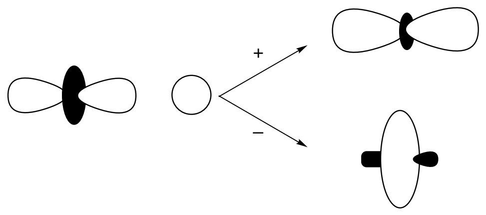

Fig. 3 Hybridization of *n*s and (*n* − 1)d_σ orbitals to decrease the antibonding nature of the $(d_\sigma)^2$ electrons in MCl_2 complexes

Table 11 Bonding in the low-lying excited states of FeCl and CoCl

	FeCl		CoCl		
State	$^6\Delta$	$^4\Delta$	$^5\Sigma^-$	$^3\Sigma^-$	$^3\Phi$
Configuration*	$(1\delta)^3(11\sigma)^1(5\pi)^2(12\sigma)^1$	$(1\delta)^3(11\sigma)^2(5\pi)^2$	$(1\delta)^4(11\sigma)^1(5\pi)^2(12\sigma)^1$	$(1\delta)^4(11\sigma)^2(5\pi)^2$	$(1\delta)^3(11\sigma)^2(5\pi)^3$
Bond order					
total	0.96	1.12	0.94	1.13	1.09
σ	0.45	0.63	0.43	0.70	0.68
π	0.51	0.49	0.51	0.43	0.41
Charge transfer/ electron					
total	0.82	0.73	0.92	0.80	0.71
σ	0.39	0.38	0.38	0.37	0.41
π	0.42	0.35	0.54	0.42	0.30

* Approximate description.

Table 12 Calculated and experimentally determined dissociation energies for FeCl, $FeCl_2$, CoCl and $CoCl_2$

		Dissociation energy/kJ mol^{-1}	
		$MCl_2 \longrightarrow MCl + Cl$	$MCl \longrightarrow M + Cl$
Fe	VWN	519	368
	BP	422	313
	Exptl.	466	330
Co	VWN	421	362
	BP	418	352
	Exptl.	426	338

$2\pi_g$ level. The bond order is approximately 20% higher than that in the ground state.

Despite the large ligand-field strength of the Cl^- ligands in these molecules, the ground states are without doubt the high-spin states. This is, at least partially, due to the stabilization of the d_σ orbital described above. Crystal-field calculations suggest a large gap between d_σ and the d_π and d_δ functions. The stabilization of the d_σ orbital results in it lying at much lower energy so that the high-spin configuration is more favourable. Interestingly, an analogous stabilization[56] of the $d_{a_{1g}}$ orbital in square-planar d^8 $[MCl_4]^{2-}$ results in a large gap between the highest-lying d orbital and the rest so helping to ensure low-spin, diamagnetic ground states.

(*b*) Monochlorides

The $^6\Delta$ ground state of FeCl and the $^5\Sigma^-$ excited state of CoCl have a single electron in both the 11σ and 12σ orbitals and this prevents effective sd hybridization so important in reducing the antibonding interaction between the σ electrons on the metal and chloride ions. In the $^4\Delta$ excited state of FeCl and the $^3\Sigma^-$ ground state of CoCl the 11σ orbital is doubly occupied and 12σ is empty. In these states sd hybridization can occur with the result that the σ contribution and the overall M–Cl bond order is increased, as shown in Table 11. Fournier[57] identified a similar balance between exchange energy and maximization of metal–ligand bonding in the monocarbonyls of the 3d transition metals.

Although in each of the states studied the metal-based 5π orbitals are doubly occupied, the repulsive role of these electrons can be seen. Thus, excitation of an electron from the 11σ to the 12σ orbital between the $^4\Delta$ and $^6\Delta$ states of FeCl and the $^3\Sigma^-$ and $^5\Sigma^-$ states of CoCl causes a lengthening of the bond but an *increase* in the π contribution to the bonding.

The ground states adopted by the monochlorides can be traced directly to the ground states of the M^+ ions. The ground state of Fe^+ is ^6D corresponding to a $4s^13d^6$ configuration. The ^4F state corresponding to a $3d^6$ configuration lies approximately 1900 cm^{-1} above this.[58] Although the $^6\Delta$ state of FeCl is more weakly bonded than the $^4\Delta$ state, it does not require excitation of the metal ion. The ground state of Co^+ is ^3F corresponding to a $3d^8$ configuration and the ^5F state corresponding to a $4s^13d^7$ configuration lies approximately 3350 cm^{-1} above this.[58] The ground state of CoCl is also a spin triplet.

(*c*) Dissociation energies

Table 12 lists the calculated dissociation energies and a comparison with the values determined experimentally by Hildenbrand.[59] The calculated values are in reasonable agreement with the experimental values although the gradient corrections used in the BP calculations appear to be required to obtain accurate energies. The most notable feature of the dissociation energies is that breaking the first bond in the dichlorides is more difficult than breaking the second. A similar pattern has been reported by Siegbahn[60] for the dihydrides, difluorides and dichlorides of the 4d transition metals.

In both the iron and cobalt systems, ionization of the metal from 1+ to 2+ leads to increased donation from the ligands and this leads to an increase in the bonding. The molecules have such low co-ordination numbers that this can be achieved without greatly increasing the intraligand repulsions. In both sets of molecules, the first ligand stabilizes the atomic configuration of the metal having the maximum number of (non-bonding) electrons in δ orbitals and the minimum number of repulsive electrons in π orbitals over the spherically symmetric atomic states. This prepares the bonding for the second ligand. In the iron chlorides, ionization of the metal from 1+ to 2+ increases the s–d energy gap stabilizing the low-spin, $3d^6$ arrangement over the high-spin, $4s^13d^5$ configuration. This allows sd hybridization to occur so reducing the repulsion experienced by the ligands and strengthening the bonding.

Acknowledgements

The author would like to thank Dr. Malcolm Gerloch for the use of the CAMMAG 4 program suite and Dr. Alain St-Amant of the University of Ottawa for making the DEFT code publicly available.

References

1 F. J. Grieman, S. H. Ashworth, J. M. Brown and I. R. Beattie, *J. Chem. Phys.*, 1990, **92**, 6365.
2 S. H. Ashworth, F. J. Grieman and J. M. Brown, *Chem. Phys. Lett.*, 1990, **175**, 660.
3 S. H. Ashworth, F. J. Grieman, J. M. Brown, P. J. Jones and I. R. Beattie, *J. Am. Chem. Soc.*, 1993, **115**, 2978.
4 S. H. Ashworth, F. J. Grieman and J. M. Brown, *J. Chem. Phys.*, 1996, **104**, 48.
5 T. Tokuda, N. Fujii, S. Yoshuda, K. Shimuza and I. Tanaka, *Chem. Phys. Lett.*, 1990, **174**, 385.
6 A. J. Bouvier, R. Bacis, J. Bonnet, S. Churasy, P. Crozet, B. Erba, J. B. Koffend, J. Lamarre, M. Lamrini, D. Pigache and A. J. Ross, *Chem. Phys. Lett.*, 1991, **184**, 133.
7 H. P. Yang, Y. Qin, Q. N. Yuan, X. B. Xie, Q. Zhuang and C. H. Zhuang, *Chem. Phys. Lett.*, 1992, **191**, 130.
8 T. Tokuda and N. Fujii, *J. Phys. Chem.*, 1992, **96**, 6504.
9 A. J. Ross, R. Bacis, A. J. Bouvier, S. Churassy, J.-C. Coste, P. Crozet and I. Russier, *J. Mol. Spectrosc.*, 1993, **158**, 27.
10 P. Crozet, A. J. Ross, R. Bacis, M. P. Barnes and J. M. Barnes, *J. Mol. Spectrosc.*, 1995, **43**, 172.
11 C. W. Bauschlicher, jun. and B. O. Roos, *J. Chem. Phys.*, 1989, **91**, 4785.
12 R. J. Deeth, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1061.
13 F. Rogemond, H. Chermette and D. R. Salahub, *Chem. Phys. Lett.*, 1994, **219**, 228.
14 A. J. Bridgeman, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2601.
15 J. T. Hougen, G. E. Leroi and T. C. James, *J. Chem. Phys.*, 1961, **34**, 1670.
16 C. W. DeKock and D. M. Gruen, *J. Chem. Phys.*, 1966, **44**, 4387.
17 D. W. Smith, *Inorg. Chim. Acta*, 1971, **5**, 231.
18 A. B. P. Lever and B. R. Hollebone, *Inorg. Chem.*, 1972, **11**, 2183.
19 A. J. Bridgeman, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4555.
20 I. Hargittai, J. Tremmel and G. Schultz, *J. Mol. Struct.*, 1975, **26**, 116.
21 E. Vajda, J. Tremmel and I. Hargittai, *J. Mol. Struct.*, 1975, **44**, 101.
22 D. W. Green, D. P. McDermott and A. Bergman, *J. Mol. Spectrosc.*, 1983, **98**, 111.
23 M. Hargittai and I. Hargittai, *J. Mol. Spectrosc.*, 1984, **108**, 155.
24 M. Hargittai, N. Y. Subbotina and M. Kolonits, *J. Chem. Phys.*, 1991, **94**, 7278.
25 D. E. Ellis, D. Guenzburger and H. B. Hansen, *Phys. Rev. B*, 1983, **28**, 3697.
26 E. L. Bominaar, J. Guillin, A. Sawaryn and A. X. Trautwein, *Phys. Rev. B*, 1989, **39**, 72.
27 R. D. Bach, D. S. Shobe, H. B. Schlegel and C. J. Nagel, *J. Phys. Chem.*, 1996, **100**, 8770.
28 K. P. Hüber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
29 M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**, Suppl. No. 1.

30 A. I. Boldyrev and J. Simons, *Periodic Table of Diatomic Molecules*, Wiley, New York, 1997.

31 J. M. Delaval and J. Schamps, *J. Phys. B: At. Mol. Phys.*, 1982, **15**, 4137.

32 C. W. Bauschlicher, *Chem. Phys.*, 1996, **211**, 163.

33 *Local Density Approximations in Quantum Chemistry and Solid-State Physics*, eds. J. P. Dahl and J. Avery, Plenum, New York, 1989.

34 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.

35 J. K. Labanowski and J. W. Andzelm, *Density Functional Methods in Chemistry*, Springer, New York, 1991.

36 T. Ziegler, *Chem. Rev.*, 1991, **91**, 651.

37 A. St-Amant, DEFT, a FORTRAN program, University of Ottawa, 1994.

38 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.

39 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

40 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

41 G. A. Medley and R. Stranger, *Inorg. Chem.*, 1994, **33**, 3976; R. Stranger, S. A. Macgregor, T. Lovell, J. E. McGrady and G. A. Heath, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4485; T. Lovell, J. E. McGrady, R. Stranger and S. A. Macgregor, *Inorg. Chem.*, 1996, **35**, 3079; J. E. McGrady, T. Lovell and R. Stranger, *Inorg. Chem.*, 1997, **36**, 3242.

42 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 1992.

43 I. Mayer, *Chem. Phys. Lett.*, 1983, **97**, 270; *Int. J. Quantum Chem.*, 1984, **26**, 151.

44 M. Gerloch, J. H. Harding and R. G. Woolley, *Struct. Bonding* (*Berlin*), 1981, **46**, 1.

45 M. Gerloch, *Magnetism and Ligand-Field Analysis*, Cambridge University Press, Cambridge, 1984.

46 A. J. Bridgeman and M. Gerloch, *Prog. Inorg. Chem.*, 1996, **45**, 179.

47 A. R. Dale, M. J. Duer, N. D. Fenton, M. Gerloch and R. F. McMeeking. CAMMAG 4, a FORTRAN program, Cambridge University, 1994.

48 G. N. Papatheodorou, in *10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases*, NBS Special Publication No. 561, 1979, vol. 1, p. 647.

49 G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, *J. Chem. Phys.*, 1962, **36**, 2879.

50 K. R. Thompson and K. D. Carlson, *J. Chem. Phys.*, 1968, **49**, 4379.

51 I. P. Alimarin, V. L. Shlenskaya and O. A. Efremenko, *Russ. J. Inorg. Chem.*, 1972, **15**, 530.

52 C. F. Putnik, G. M. Cole, jun., B. B. Garrett and S. L. Holt, *Inorg. Chem.*, 1976, **15**, 826.

53 J. Ferguson, D. L. Wood and K. Knox, *J. Chem. Phys.*, 1963, **39**, 881.

54 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, 1961, **83**, 4690.

55 G. Herzberg, *Electronic Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, 1966.

56 A. J. Bridgeman and M. Gerloch, *Mol. Phys.*, 1993, **79**, 1195.

57 R. Fournier, *J. Chem. Phys.*, 1993, **99**, 1801.

58 C. E. Moore, *Atomic Energy Levels Volume II*, Circular of the National Bureau of Standards 467, 1952.

59 D. L. Hildenbrand, *J. Chem. Phys.*, 1995, **103**, 2634.

60 P. E. M. Siegbahn, *Theor. Chim. Acta*, 1994, **87**, 441.

Received 25*th June* 1997; *Paper* 7/04478J