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Electron Paramagnetic Resonance of Tetrakis(1-norbornyl)chromium[1]

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Received August 23, 1973

Single-crystal epr of (nor)$_4$Cr showed the molecule to have an isotropic g factor for the $\Delta m = 1$ transition. There were no $\Delta m = 2$ and double-quantum transitions; therefore $D \approx E \approx 0$. In most organic glass these transitions become allowed. (nor)$_4$Cr apparently assumes several conformations in isooctane and cyclohexane glasses which are distinguishable by their zero-field splitting parameters. Among all the solvents examined benzene perturbs the ligand field symmetry the least. Only a weak $\Delta m = 2$ signal was occasionally detected; there was no double-quantum transition even at highest available microwave power.

Introduction

A few tetravalent chromium compounds are known until recently. $CrCl_4$ and $CrBr_4$ are gaseous materials and CrF_4 is a greenish black solid.[3] K, Rb, and Cs salts of CrF_6^{2-} have been reported;[3] $SrCrO_4$ and $BaCrO_4$ are found to be complex mixed oxides.[4] A few $Cr(OR)_4$ compounds (R = CMe_2Et, $CMeEt_2$, CEt_3, and $SiEt_3$) have been synthesized[5,6] which are relatively stable, a fact attributable to the absence of α-CH bonds. A number of stable CrR_4 compounds (R = *t*-Bu, *n*-Bu, neopentyl, CH_2CEt_3, CH_2CMe_2Ph) have been prepared.[7] Their relative stability is largely due to the absence of β-CH bonds. The compounds are even stable toward attacks by oxygen and aqueous H_2SO_4 when R = 1-norbornyl (nor) and 4-camphyl.[8] It is believed that the bulky space-filling ligands protected the attack of the metal-carbon bond by most reagents. We have begun a systematic investigation of the structure and reactions of these compounds. In this paper the electron paramagnetic resonance, epr, results for (nor)$_4$Cr are presented.

Magnetic susceptibility measurements on $Cr(OR)_4$ and CrR_4 gave magnetic moments which are close to the spin-only value for a triplet d^2 system.[6,8] They, however, differ significantly in their relaxation times. For example, epr was undetectable for $Cr(O\text{-}t\text{-}Bu)_4$ down to 98°K.[6] At 10°K a $\Delta m = 1$ transition was seen at $g = 1.962$ and a broad $\Delta m = 2$ transition at half-field. On the other hand, CrR_4 shows a room-temperature $\Delta m = 1$ signal as well as a narrow $\Delta m = 2$ resonance at lower temperatures.[9] The spectra of (nor)$_4$Cr are more interesting than all the other derivatives because of the extreme sensitivity to the environment. These results are described below.

Experimental Section

Synthesis of 2,2-Dichloronorbornane. The following procedure was adapted from Bixler and Niemann[10] and Newman and Wood.[11] A 500-ml three-necked flask was placed inside a 4-l. beaker and equipped with a paddle stirrer. The entire assembly was put into a glove bag for overnight drying in the presence of a beaker of P_2O_5. A 0.38-mol amount of PCl_3 (Baker) was charged into the flask, after which a $CaSO_4$ drying tube was inserted. The large beaker was packed with a salt-ice mixture to cool PCl_3 to −10°. Norcamphor, 0.45 mol (Aldrich), was then added in five portions over a 45-min period. A total of 0.514 mol of PCl_5 (Baker) was next introduced in five aliquots. The reaction mixture was allowed to stand overnight and then poured over 588 g of ice. This was followed by adding 600 ml of pentane (Matheson Coleman and Bell Practical grade). After 75 min, the reaction mixture was brought to ambient temperature. The yellow organic phase was separated and dried over anhydrous Na_2SO_4, and pentane was removed by rotary evaporation. Distillation at 88° and 23 mm gave 53.0 g of product at a 72% yield. The infrared spectrum of the product showed the absence of norcamphor. The nmr spectrum of the product in $CDCl_3$ has peaks and intensities expected for 2,2-dichloronorbornane.

Synthesis of 1-Chloronorbornane. The conversion of 2,2-dichloronorbornane is accomplished by a Wagner-Meerwein reaction and hydrogen-halogen exchange as described by Bixler and Niemann[10] and Bartlett, *et al.*[12] Pentane was purified by concentrated H_2SO_4; the colored acid was removed after overnight stirring. The process was repeated until the acid remained clear after 18 hr. The pentane was washed twice, neutralized, washed once more before drying over anhydrous $MgSO_4$, and distilled over $AlCl_3$.

A 0.27-mol amount of 2,2-dichloronorbornane was dissolved in 800 ml of purified pentane in a 2-l. three-necked flask which was equipped with an HCl trap and a paddle stirrer. A 0.126-mol sample of $AlCl_3$ was weighed into a 50-ml erlenmeyer flask and added in four portions over 2.5 hr. The mixture was allowed to stand for 38 hr with occasional stirring. The supernatant organic layer was decanted and the red-brown oil was extracted with two 300-ml aliquots of hexane previously dried over $MgSO_4$. The pentane and hexane solutions were combined, washed with 500 ml of water, and neutralized with 500 ml of saturated $NaHCO_3$ solution. The solvent was removed at room temperature and the product was distilled at 73° (56 mm) (reported bp 70° (54 mm)). The yield was 14.6 g (41.3%).

Synthesis of Tris(tetrahydrofuran)chromium Trichloride. The basic procedure of Herwig and Zeiss[13] was followed closely to give a yield of 54.7%.

Synthesis of Tetrakis(1-norbornyl)chromium. In this synthesis 1-norbonyllithium was prepared by a procedure adapted from those described by Bixler and Niemann[10] and Winstein and Traylor.[14] The product was, however, not isolated, but used directly to synthesize (nor)$_4$Cr.

Hexane was purified with concentrated H_2SO_4 as described above for pentane except final distillation was from $LiAlH_4$.

A 500-ml three-necked flask was charged with 100 ml of 6-mm borosilicate glass beads and 40 ml of purified hexane. The flask was equipped with a paddle stirrer and a reflux condenser which was connected through P_2O_5–$CaCl_2$ and $CaCl_2$ drying tubes to an argon inlet and a vent. A Y adapter was inserted in the third neck. A bent tube containing 4.1 g of $CrCl_3$ was attached to one joint of the adapter; to the other joint was connected a dropping funnel containing 5.1 g of 1-norbonyl chloride dissolved in 40 ml of hexane, a reflux condenser, and an Hg bubbler. One gram of Li metal (Foote) was rinsed in pentane, cut into tiny pieces under Ar, and introduced quickly into the reaction mixture. This was heated under a slight

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[1] Presented at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 15, 1973.

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Table I. Epr Data for $(nor)_4Cr$ in Various Solutions

		$\Delta m = 1$			$\Delta m = 2$		
			Line width, G			Line width, G	Double-quantum transition
Solvent	Mp, °C	*g*	25°	−196°	*g*	−196°	
2-Methylheptane	−109	1.990	20	190	3.962	11	+
2,2-Dimethylheptane	−116	1.988	20	192	3.962	11	+
2,2,5-Trimethylhexane	−106	1.991	20	200	3.960	13	+
n-Heptane	−91	1.988	19	170	3.960	12	+
Ethylbenzene	−94	1.989	*a*	180	*a*		+
Isobutylbenzene	−515	1.989	*a*	180	*a*		*a*
2-Methylpentane	−153.7	1.987	20	157	*a*		+
Cyclohexene	−103.5	0.986	19	250	*a*		+
Isooctane	−107.4	1.987	18	zfs[b]		mr[c]	+
Cyclohexane	6.5	1.986	19	zfs		mr	+
Benzene	5.5	1.986	21	60	Weak		−

[a] Measurement not made. [b] Zero-field splitting. [c] Multiple resonances.

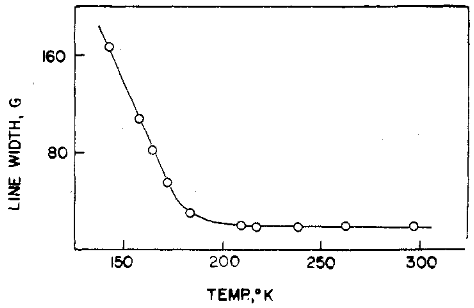

Figure 1. Variation of $\Delta m = 1$ line width with temperature of $(nor)_4Cr$ 0.32 m*M* in isooctane.

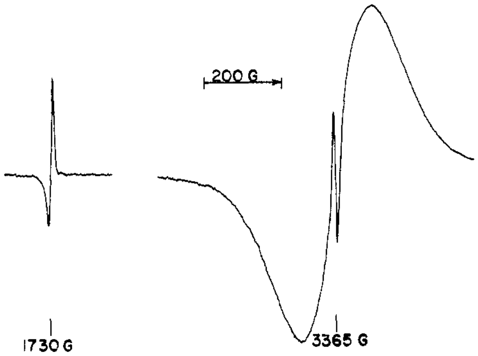

Figure 2. Epr spectrum of $(nor)_4Cr$ 3.1 m*M* in 2,2-dimethylheptane at 93°K.

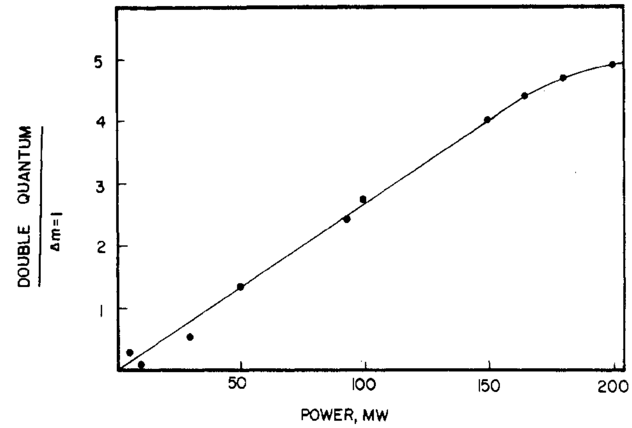

Figure 3. Signal peak:height ratio of the double-quantum transition to the $\Delta m = 1$ transition as a function of microwave power for $(nor)_4$-Cr 1.1 m*M* in 2,2,5-trimethylhexane.

Ar pressure. The hexane solution of 1-chloronorbornane was added in three 15-ml portions over 1.5 hr and followed by 2 hr of refluxing. $CrCl_3 \cdot 3THF$ was dumped quickly into the flask and stirred for 20 hr. The liquid was separated from the beads and the pentane solubles were separated by centrifuging and decanting. The insoluble materials were washed twice with 30-ml portions of pentane. The pentane solution was passed through a column of alumina (Brockmann No. 1, 21 cm × 2 cm). Pentane was removed on a rotary evaporator yielding 2.1 g of $(nor)_4Cr$ (44% yield).

Epr Measurements. The following solutions of $(nor)_4Cr$ were prepared: 0.32 and 10 m*M* in isooctane, 3.1 and 0.39 m*M* in 2,2-dimethylheptane, 3.1 m*M* in 2-methylheptane, 0.44 m*M* in benzene, 1.1 m*M* in 2,2,5-trimethylhexane, 1.4 m*M* in *n*-heptane, 1.4 m*M* in ethylbenzene, 1.85 m*M* in isopropylbenzene, 2.32 m*M* in isobutylbenzene, 1.6 m*M* in cyclohexene, 1.85 m*M* in cyclohexane, and 1.5 m*M* in 2-methylpentane. All the solutions were evacuated and sealed unless otherwise stated.

Results and Discussion

The epr spectrum of $(nor)_4Cr$ solutions at ambient temperature is a simple symmetric resonance with a half-width of about 20 G (Table I). The *g* value ranges from 1.986 to 1.990. The $\Delta m = 1$ resonance was not saturated up to a microwave power of 200 mW.

In most solvents, the spectra have the same line shape and width as temperature is lowered except for the expected increase in intensity. Beginning at about 200°K, line broadening occurs. Figure 1 shows the increase of line width with the decrease of temperature.

It is at low temperatures that the epr spectrum of $(nor)_4$-Cr becomes very sensitive to the environment (Table I).

In most solvents, except isooctane, benzene, and cyclohexane, the spectrum of $(nor)_4Cr$ consists of a broad (157-250 G) $\Delta m = 1$ transitions, a narrow (11-13 G) $\Delta m = 2$ transition at half-field, and a spike at $g \sim 2$ (Figure 2). The two latter resonances usually appear at the same temperature. For example, if the solution is cooled slowly from 298°K, they appear at *ca.* 163°K. If the sample is warmed from 93 to 200°K and then cooled, these two resonances often become detectable at 128°K. At 93°K, saturation studies showed that the $\Delta m = 1$ transition increases in line width without significant enhancement of peak height as microwave power in increased. It becomes saturated at 30 mW. In contrast, the spike at $g \sim 2$ increases with the increase of microwave power so that its signal height relative to that of the $\Delta m = 1$ transition increases linearly with power (Figure 3). The spike is attributable to the double-quantum transition.[15,16]

It will be shown later that $(nor)_4Cr$ has an isotropic *g* factor. The appropriate spin Hamiltonian is

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$$\begin{aligned}\mathcal{H} &= \beta HgS + D(S_z^2 - {}^1/_3S^2) + E(S_x^2 - S_y^2) \\ &= \beta HgS - (XS_x^2 + YS_y^2 + ZS_z^2)\end{aligned} \qquad (1)$$

where the zero-field splitting parameters D and E are related to the principal values of the dipolar tensor X, Y, and Z by the relationships

$$\begin{aligned}D &= {}^1/_2(X + Y) - Z \\ E &= {}^1/_2(Y - X)\end{aligned} \qquad (2)$$

Furthermore, $X + Y + Z = 0$. When $E = 0$ and $D \neq 0$, the $\Delta m = 1$ transition consists of two pairs of lines. The inner pair is separated by $D/g\beta$; the separation between the outer pair is twice as much.[17] When both D and E are different from zero, there should be three pairs of lines centered about midfield with separations of $(D - 3E)/g\beta$, $(D + 3E)/g\beta$, and $2D/g\beta$.

The spin wave functions with the magnetic field along the z axis are

$$\begin{aligned}|\Psi_x\rangle &= \cos\theta\,|\alpha\alpha\rangle - \sin\theta\,|\beta\beta\rangle \\ |\Psi_y\rangle &= \sin\theta\,|\alpha\alpha\rangle + \cos\theta\,|\beta\beta\rangle \\ |\Psi_z\rangle &= \frac{1}{\sqrt{2}}\,|\alpha\beta + \beta\alpha\rangle\end{aligned} \qquad (3)$$

where

$$\tan 2\theta = (X - Y)/2g\beta H \qquad (4)$$

The intensity of the $\Delta m = 2$ transition is determined by the square of the matrix element

$$\langle\Psi_x|S_z|\Psi_y\rangle = \sin 2\theta = -2E/\delta \qquad (5)$$

where $\delta = h\omega$ is the quantum of microwave photon.

The resonance fields for the $\Delta m = 2$ transitions are[16]

$$\begin{aligned}H_x &= (1/2g\beta)[\delta^2 - (D + E)^2]^{1/2} \\ H_y &= (1/2g\beta)[\delta^2 - (D + E)^2]^{1/2} \\ H_z &= (1/2g\beta)[\delta^2 - E^2]^{1/2}\end{aligned} \qquad (6)$$

The most prominent resonance in the $\Delta m = 2$ region is located at H_{min}

$$H_{\text{min}} = (1/2g\beta)[\delta^2 - 4/3(D^2 + 3E^2)]^{1/2} \qquad (7)$$

The anisotropy is smallest for those molecules whose orientations are such that their resonant fields are in the neighborhood of H_{min}.

The double-quantum transition results from the excitation of the $m_s = -1$ ground state by two microwave photons to the $m_s = +1$ state. The process is not easily saturated. The value of the resonance field H_r as a function of molecular orientation θ and φ is given by[16]

$$\begin{aligned}&X\sin^2\theta\,\text{cis}^2\,\varphi + Y\sin^2\theta\sin^2\varphi + Z\cos^2\theta = \\ &\quad (g\beta H_r)^{-2}[XYZ \pm {}^1/_9(\delta^2 - (g\beta H_r)^2 - {}^1/_3D^{*2}) \times \\ &\quad (12(g\beta H_r)^2 - 3\delta^2 + 4D^{*2})^{1/2}]\end{aligned} \qquad (8)$$

where

$$D^{*2} = D^2 + 3E^2 \qquad (9)$$

The probability of the transition is large only when the energy differences between the two pairs of adjacent levels are nearly equal. The condition is satisfied if

$$\delta^2 - (g\beta H_r)^2 - {}^1/_3D^{*2} = 0 \qquad (10)$$

in eq 8. Of course when $D = E = 0$, the double-quantum transition is indistinguishable from the $\Delta m = 1$ transition.

In this first group of solvents the $\Delta m = 2$ signal corresponds to the H_{min} resonance. For instance in 2-methylheptane the resonance field is 1663.3 G at 9.25 GHz and $2g\beta H_{\text{min}} = \delta$. The $\Delta m = 1$ resonance is devoid of zero-field splitting. Two explanations are possible. Either both D and E are extremely small or the molecule fluctuates between conformations differing in zero-field splittings at a rate exceeding 5×10^8 sec^{-1}. It will be shown that the latter possibility is the more probable one.

There is a certain amount of variability in the epr spectra of (nor)$_4$Cr. The line width of the $\Delta m = 2$ transition can range from 10 to 20 G and that of the $\Delta m = 1$ resonance from 183 to 260 G. The intensities of all the transitions are also dependent upon the thermal history of the sample. On the other hand, as far as it can be ascertained, the spectrum is not affected by oxygen and is independent of concentration. The bulky and space-filling ligand presents an impervious barrier to oxygen and also reduces dipolar broadening to a minimum.

The epr spectra of isooctane and cyclohexane differ from those described above only at the low-temperature limit. A typical spectrum at 93°K for the $\Delta m = 1$ transition for isooctane solutions is shown in Figure 4. The zero-field splitting features are quite reproducible; the realtive intensities and resolutions however vary from one run to another. These characteristics become obliterated between 128 and 158°K depending upon the thermal history. The multitude of lines can only be due to (nor)$_4$Cr molecules frozen in different conformations with different zero-field splittings. In analyzing the spectrum we assumed each conformation to have nonzero D and E values. Starting from the outermost resonances which was assumed to have a separation of $2D/g\beta$ for conformation I, we seek two pairs of lines which have separations of $(D \pm 3E)/g\beta$. After locating this first set of lines, the procedure was repeated for the next outermost pair of resonances and so on. In this manner we can account for the observed spectrum (Figure 4) with four conformations for (nor)$_4$Cr in isooctane glass. The results are summarized in Table II.

The spectrum of a cyclohexane solution of (nor)$_4$Cr in this region is similar to that of an isooctane solution but is poorer in resolution by comparison.

In the half-field region three signals were found at 1613, 1648, and 1661.5 G in isooctane (Figure 5). The H_{min} for the four conformations calculated from the zero-field parameters in Table II are 1658, 1660, 1662, and 1665 G. In cyclohexane four $\Delta m = 2$ resonances are clearly resolved at 1526, 1586, 1614, and 1638 G (Figure 6). The poor agreement suggests that there may be in the $\Delta m = 1$ region weaker outlying lines which are not resolved. These would increase the zero-field splitting parameters.

Single crystals of (nor)$_4$Cr (orthorhombic) were mounted on a two-circle goniometer the design of which was described elsewhere.[18,19] At room temperature the spectrum is symmetric; $g = 1.9905$ and line width ≈ 40 G. This spectrum does not change with rotation of the crystal in the magnetic field about all three crystallographic axes. The value of E must be very small (10^{-3} cm^{-1}). Although the $\Delta m = 1$ resonance was saturated at 30 mW and 77°K, the double-

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Table II. Zero-Field Splitting Parameters for $(nor)_4Cr$ in Isooctane at 93°K

Con-formn	D, cm^{-1}	E, cm^{-1}	Con-formn	D, cm^{-1}	E, cm^{-1}
I	0.027	0.0041	III	0.013	0.0032
II	0.023	0.0027	IV	0.012	0.0029

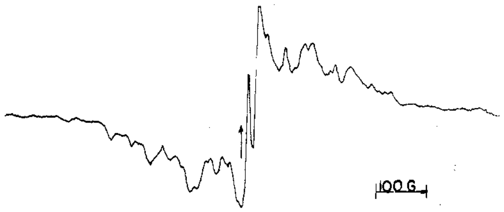

Figure 4. Epr spectrum of $(nor)_4Cr$ 0.32 m*M* in isoctane at 77°K, $\Delta m = 1$ transition. Marker is for DPPH.

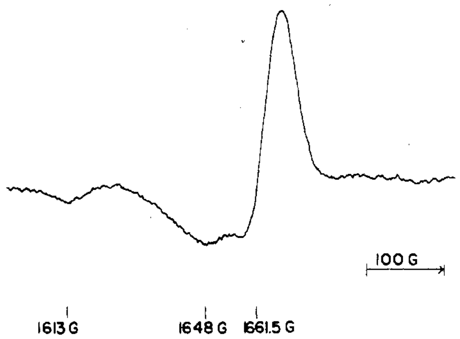

Figure 5. Epr spectrum of $(nor)_4Cr$ 0.32 m*M* in isooctane at 77°K, $\Delta m = 2$ transition.

quantum transition was not observed even at 200 mW. This situation is only possible if $D \approx -3E$ in eq 10.

Since isooctane was the first solvent noted by us to perturb the symmetry of the $(nor)_4Cr$ molecule, several other solvents were examined. Their choice was based on structural similarities to isooctane. Therefore, 2,2-dimethylheptane resembles one end of the isooctane molecule and 2-methylheptane and 2-methylpentane resemble the other end. It is only in the case of 2,2-dimethylheptane that there is a hint of zero-field splitting of its $\Delta m = 1$ transition. Apparently, there is no relationship between the shape of the solvent molecule and its effect on the zero-field splitting of $(nor)_4Cr$. Also most of the alphatic hydrocarbons probably have the same glass transition temperatures of 80-90°K.[20] According to the significant structure theory of liquids[21] the viscosities of these glasses would be comparable. It is possible that the phenomenon described here is of a local nature.

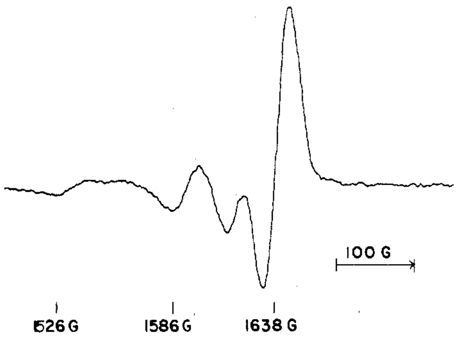

Figure 6. Epr spectrum of $(nor)_4Cr$ 1.85 m*M* in cyclohexane at 77°K, $\Delta m = 2$ transitions.

Acknowledgment. This work was supported by Grant No. GH 39111 from the National Science Foundation.

Registry No. $(nor)_4Cr$, 36333-78-5; 2,2-dichloronorbornane, 19916-65-5; 1-chloronorbornane, 765-67-3; $CrCl_3 \cdot 3THF$, 10170-68-0.

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Syntheses, Infrared Spectra, Magnetic Properties, and Electronic Structures of Di-μ-oxo- and Di-μ-oxo-bis(di-μ-oxo)-Bridged Oxomolybdates(V) and Their Theoretical Interpretation

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Received May 1, 1973

The studies of several dimeric and tetrameric oxomolybdates(V) are reported. By the appropriate synthesis routes double-bridged di-μ-oxo-bis[oxomolybdates(V)], μ-oxo-μ-(sulfato,perchlorato,oxalato)-bis[oxomolybdates(V)], and tetrameric di-μ-oxo-bis[di-μ-oxo-oxodimolybdates(V)] were obtained. The character of molybdenum-oxygen bonding is discussed in detail, based on the normal-coordinate analysis carried out for the dimeric di-μ-oxo-bridged oxomolybdates(V) and for a simplified model of the oxomolybdate(V) tetramers. The electronic structure calculations for the dimeric double-bridged $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ and single-bridged $[Mo_2O_3(NCS)_8]^{4-}$ complexes, carried out by the SCCC MO and angular overlap methods, respectively, are reported. On the basis of these results the origin of the spin pairing in polymeric oxomolybdates(V) is discussed in detail.

Introduction

Metal-metal interaction has become the subject of intensive studies in recent years.

Depending on the geometrical configuration of a molecule and on the electronic structure of a metal ion, the metal-metal interaction between paramagnetic ions could be weak (exchange interaction) or strong (bonding interaction), indirect (interaction involving the diamagnetic atoms or