Theoret. chim. Acta (Berl.) 12, 293—306 (1968)

Electronic Structure of Octacyanides of Molybdenum IV and V According to the SCCC MO Method

The D_{4d} Case

A. GOŁĘBIEWSKI and H. KOWALSKI

Department of Theoretical Chemistry, Jagiellonian University, Cracow, Poland

Received February 9, 1968/August 7, 1968

The SCCC MO method has been used to calculate the electronic structure and spectrum of $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ ions of a D_{4d} symmetry. All metal-ligand and ligand-ligand interactions and all overlap integrals (over products of HF atomic orbitals) have been included within the SCCC MO scheme. Basing on these calculations a new assignment of some absorption bands is proposed. The overall agreement between the calculated and observed electronic spectrum is satisfactory.

Elektronenstruktur und Spektrum der $[Mo(CN)_8]^{-4}$- und $[Mo(CN)_8]^{-3}$-Ionen in D_{4d}-Symmetrie wurden mit der SCCC-MO-Methode berechnet. Alle Metall-Ligand- und Ligand-Ligand-Wechselwirkungen und Überlappungsintegrale wurden berücksichtigt. Die Bandenzuordnung wurde neu vorgenommen. Die Übereinstimmung der berechneten und gemessenen Spektren ist befriedigend.

Application à $Mo(CN)_8^{4-}$ et $Mo(CN)_8^{3-}$ de la méthode SCCC MO basée sur des orbitales atomiques HF approchées, en tenant compte du recouvrement et de toutes les interactions ligand-ligand. Dans la partie I on discute le cas de la symétrie D_{4d}. L'accord global avec l'expérience est satisfaisant en ce qui concerne les spectres. On montre aussi que toutes les attributions antérieures basées sur la théorie du champ cristallin semblent inadéquates.

1. Introduction

The structure of octacyanide ions of molybdenum IV and V seems not yet to be established. According to the X-ray analysis of $K_4Mo(CN)_8$ the anion should have a D_{2d} (or, strictly, C_s) symmetry [17–19]. On the other hand, according to some early IR and Raman works the symmetry of the $Mo(CN)_8^{4-}$ anion in solutions should be D_{4d} [42–43]. However, a recent analysis of the IR spectrum does not confirm this result [36]. The NMR analysis does also give no preference [33]. A more definite information was obtained with the use of the EPR method [10, 12, 16, 45, 46]. Analyzing the EPR spectrum of $Mo(CN)_8^{3-}$ ions in solutions Garvey [10] and Hayes [16] have found the experimental data to be incompatible with the assumption of D_{2d} symmetry and compatible with the assumption of D_{4d}. Unexpectedly however, the EPR spectrum of the $Mo(CN)_8^{3-}$ ions shows a qualitative change if a $K_4Mo(CN)_8$ solid matrix is used [10]. The change of the spectrum indicates a change of the symmetry of the $Mo(CN)_8^{3-}$ ion from D_{4d} to D_{2d}.

A photoproduct of octacyanides of molybdenum IV was discovered and isolated by Jakób *et al.* [21–24] which was originally claimed to have the formula $Cd_2Mo(CN)_8(N_2H_4)_2$. However, J. Chojnacki *et al.* carried out an X-ray analysis of this compound, the results being in the course of publication. It was found that $Mo(CN)_8^{4-}$ units can be distinguished which have (approximately) a D_{4d} local symmetry. The N_2H_4 ligands lie farther apart.

According to theoretical speculations of some authors [33, 27] a dynamical equilibrium of both structures of the $Mo(CN)_8^{q-}$ ions takes place. However, such an equilibrium has to be strongly shifted towards one of the structures. Otherwise the observed changes of the spectrum of $Mo(CN)_8^{3-}$ in the EPR region, depending on the medium, would be hard to explain.

One could claim that the structure of $Mo(CN)_8^{q-}$ ions is different in solutions and in the pure solid state. It is unlikely as the absorption spectra in the UV and visible regions are highly similar [28].

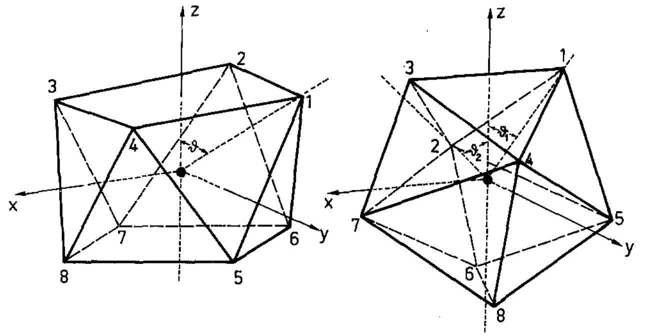

Fig. 1. Two possible structures of octacyanides of molybdenum

In conclusion we expect that:

i) $Mo(CN)_8^{3-}$ ions are likely to have the D_{4d} symmetry, both in solutions and in the pure solid state;

ii) yellow $Mo(CN)_8^{4-}$ ions are likely to have the D_{2d} symmetry, both in solutions and in the pure solid state;

iii) red $Mo(CN)_8^{4-}$ units in the Jakób compound are likely to have the D_{4d} symmetry, both in solutions and in the pure solid state.

The two controversial structures are illustrated in Fig. 1. Let us note that several other complexes of the D_{4d} symmetry are known, the ϑ angle (see Fig. 1 for definition) ranging from 57° to 59° [26]. A hard sphere model reproduces the structure of these complexes fairly well yielding $\vartheta = 59.4°$. Also several complexes of the D_{2d} symmetry are known, with the ϑ_1 angle (Fig. 1) ranging from 35.2° to 36.4° and the ϑ_2 angle (Fig. 1) ranging from 71.8° to 75° [26]. The hard sphere model works fairly well again, yielding $\vartheta_1 = 36.85°$ and $\vartheta_2 = 69.46°$.

Early theoretical works were based on the concept of Pauling's hybride strengths with a relative bonding power of metal *s*, *p* and *d* valence orbitals equal to 1, $\sqrt{3}$, and $\sqrt{5}$ accordingly. Assuming an integer occupation number of the metal *s* valence orbital one finds that $\vartheta = 60° 54'$, $\vartheta_1 = 34° 33'$, and $\vartheta_2 = 72° 47'$ [38]. These theoretical results are in a remarkable agreement with experiment. Allowance for fractional occupation numbers makes the agreement with experiment still better, yielding for example $\vartheta = 59° 16'$ [7]. However, the difference of hybride strengths for the two structures is negligible [13].

The absorption spectra of octacyanide ions of molybdenum IV and V in the visible and UV regions have been also a subject of a repeated analysis. Crystal field theory (CFT) was mostly used with this purpose. Aside from few preliminary notes [14, 15, 35, 39] the following treatments may be referred to:

i) the CFT treatment of the D_{4d} case by Gliemann [11] and König [28] and in a modified form by one of the authors *et al.* [24];

ii) the CFT treatment of the D_{2d} case by Golding and Carrington [12] and, very recently, by Basu *et al.* [4];

iii) the ligand field treatment of the C_s case (a distorted D_{2d} case) by Perumareddi, Liehr and Adamson [37].

Surprisingly all these authors obtained an excellent agreement with experiment. However, apart from some other details, Golding and Carrington have missed some absorption bands experimentally. Also the experimental spectra found by Basu *et al.* are not always the same as those found by other authors. Perumareddi *et al.*, on the other hand, assumed a strong distortion of the dodecahedron towards the C_s symmetry. Such a strong distortion is not likely to take place at least in the case of solutions. Besides, these authors used a fixed set of crystal field splitting parameters, independent of the oxidation state of molybdenum. However, such a dependence cannot be ignored [25]. Gliemann and König, on the other hand, predicted an unlikely low lying triplet state in the case of the $Mo(CN)_8^{4-}$ ions. Also their interpretation of the most intensive absorption bands as due to double excitations of electrons was criticized [37]. Their antiprism was a twisted cube with $\vartheta = 54.7°$, the ϑ angle being too low by some 5°. Allowing for a proper flattening of the antiprism it was possible to remove the low lying triplet state keeping the overall good agreement with experiment [24]. The questions of intensity, however, remained still unsolved.

Undoubtedly the crystal field theory is hardly a satisfactory approach in the case of cyanides. Its apparent success achieved by König, Golding and Carrington and the other authors was mainly due to the fact that the empirical parameters have been chosen as to fit the spectrum. Molecular orbital calculations with no parameters chosen to fit the spectrum, even if approximate, should yield more information. A qualitative discussion of the MO approach is already known [5], but a quantitative is still lacking. For this reason we decided to analyze the octacyanides of molybdenum IV and V in terms of the SCCC MO modification [1, 3, 30, 31] of the Wolfsberg and Helmholz method [47]. The SCCC MO procedure was not always successful in the past [8, 20], overestimating the covalency. However, such an overestimation seems not to be essential in the case of cyanides. Indeed, a substantial success was achieved by some authors in the case of metal pentacyanonitrosyls [30, 31]. Thus we could expect that a SCCC MO approach to octacyanides might be useful.

In the present work we consider the D_{4d} case of $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$. The D_{2d} case and a comparative study of the two symmetries is postponed to a later publication.

2. Methods of Calculation

The details of the SCCC MO procedure are described in several places [1, 3, 30, 31, 44]. Therefore we draw only attention to some minor changes in the standard procedure and to the choice of wave functions and empirical parameters.

The population analysis was carried out for Löwdin's orthogonalized atomic orbitals [29]. In the standard procedure the Mulliken population analysis is commonly used [34]. However, orthogonalized orbitals are better localized than ordinary orbitals and therefore seem to be better suited for this purpose [9]. Anyhow, the expected differences in populations are not large [9]. Also a different interpolation formula for the values of the valence orbital ionization potentials (VOIP's) was used,

$$\mathrm{VOIP}(l) = \sum_{j,k=0}^{2} a(l,j,k)\, Q^j \frac{n_k}{n_0 + n_1 + n_2} \tag{1}$$

where n_0, n_1, n_2 are the populations of the $5s$, $5p$, and $4d$ orbitals respectively, Q is the effective charge of the central atom in atomic units and $l = 0$ for $5s$ electrons, $l = 1$ for $5p$ electrons and $l = 2$ for $4d$ electrons.

Determining the elements $a(i,j,k)$ in Eq. (1) we have taken into account all assigned atomic levels of Mo(I) – Mo(V) which have been available [32, 40]. The average orbital energies have been estimated in a way described for example by Gray and Ballhausen [1]. Provided the VOIP values are given in kK the values of the $a(l,j,k)$ are as follows: 103.2, 187.2, 46.8, 62.0, 16.0, 53.0, 10.7, 12.7, 0.0, 81.9, 81.9, 27.3, 54.55, 54.55, 30.45, 1.75, 1.75, 8.45, 145.4, 231.2, 48.2, 47.4, –34.8, 66.7, 16.6, 32.5, 8.0. The elements are given in the order $a(0,0,0)$, $a(0,0,1)$, $a(0,0,2)$, $a(0,1,0)$, etc. The VOIP values for the electrons of CN^- have been chosen as by Manoharan and Gray: 112.9 kK for σ-electrons, 122.0 kK for π-bonding electrons and 30.0 kK for π^*-antibonding electrons.

Resonance integrals have been approximated according to the Wolfsberg and Helmholz formula, $H_{kl} = F_{kl} \frac{H_{kk} + H_{ll}}{2} S_{kl}$, where $F_{kl} = F_\sigma = 2.2$ for σ-type bonding with the central atom, $F_{kl} = F_\pi = 2.0$ for π-type bonding with the central atom and $F_{kl} = F_{\mathrm{lig}} = 2.1$ for interactions between the ligands. The F_σ and F_π values are the same as those used by Manoharan and Gray in their treatment of pentacyanonitrosyls.

Overlap integrals have been calculated with the use of approximate $5s(\mathrm{Mo}^+)$, $5p(\mathrm{Mo}^+)$, $4d(\mathrm{Mo}^+)$ Hartree-Fock atomic orbitals [2] and approximate $\sigma(\mathrm{CN}^-)$, $\pi(\mathrm{CN}^-)$, $\pi^*(\mathrm{CN}^-)$ SCF LCAO molecular orbitals [30]. More accurate Hartree-Fock atomic orbitals exist for Mo^+ [41]. The use of them, however, owing to the limitations of the SCCC MO method, would be an unnecessary complication. Carrying out these integrations the following interatomic distances and bond angles have been assumed: $R(\mathrm{Mo{-}C}) = 4.0800$ a.u. [17], $R(\mathrm{C{-}N}) = 2.191$ a.u. [30], $\measuredangle(\mathrm{Mo{-}C{-}N}) = 180°$, $2\vartheta = 118° 52'$. The last value follows from the hard sphere model [26]. It is sufficiently close to the average experimental values of 2ϑ, reducing on the other hand the number of different integrals by about $\frac{1}{4}$.

The overlap integrals have been calculated on a Gier computer, using a program written by one of us (A.G.). The program was checked for several literature values taking corrections, where necessary [6]. Also the SCCC MO iteration procedure was carried out on the Gier, using an automatic program written by one of us (A.G.).

The orientation of cyanides σ and $\pi(\pi^*)$ molecular orbitals has been chosen as shown in Fig. 2. From the nine metal valence orbitals, 8 nonbonding σ orbitals of the CN^- groups, 16 bonding π orbitals of these groups and 16 antibonding π^* orbitals altogether 49 molecular orbitals can be constructed. Their symmetry classification for the D_{4d} group is as follows: $5a_1$, $2a_2$, $2b_1$, $4b_2$, $6e_1$, $6e_2$, and $6e_3$, the notation of irreducible representations being the same as Gliemann's.

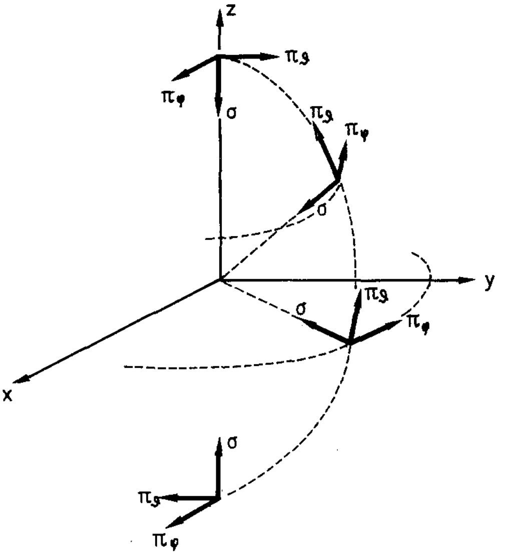

Fig. 2. Orientation of σ, π_ϑ, and π_φ-type ligand orbitals

3. Electronic Configuration of $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ Ions

The calculated molecular orbital energies (except for a few states of high and low energies) are listed for both anions in Table 1. To save space we do not quote the eigenvectors. We are willing to send them on individual request. Instead, we quote the constituent metal and ligand orbitals which give the main contribution to the molecular orbital. For example $e_3(\pi^*_\vartheta > \pi^*_\varphi)$ means that the appropriate e_3 molecular orbital has a main contribution from π^*_ϑ ligand orbitals, a smaller contribution from π^*_φ ligand orbitals and more or less negligible contributions from other orbitals.

We see from Table 1 that exactly 5 molecular orbitals exist in which the $4d$ molybdenum orbitals are dominating. Thus they correspond to the splitted $4d$ orbitals of the CF theory. Lowest is the $a_1(d)$ level with an 86–88% contribution from the $4d_{z^2}$ level of the central atom (Table 2). Contribution of ligand π-bonding and π^*-antibonding levels is small although comparable (7–10% and 5–4% respectively). The other two "d" levels are strongly antibonding with a 32–41% contribution from ligand σ-levels, depending on oxidation state of the molybdenum atom, and a negligible contribution ($\leqq 7\%$) from the ligand π and π^* levels. As the populations for the "d" levels may raise some general interest we list them in Table 2.

Table 1. *Orbital energies in* $Mo(CN)_8^{3-}$ *and* $Mo(CN)_8^{4-}$

$Mo(CN)_8^{3-}$		$Mo(CN)_8^{4-}$	
Energy (kK)	Description of the orbital	Energy (kK)	Description of the orbital
⋮		⋮	
− 26.38	$e_1(\pi_\varphi^*)$	− 26.36	$e_1(\pi_\varphi^*)$
− 26.85	$a_1(\pi_\vartheta^*)$	− 27.23	$a_1(\pi_\vartheta^*)$
− 28.00	$e_2(\pi_\varphi^*)$	− 28.01	$b_2(\pi_\vartheta^*)$
− 28.22	$b_2(\pi_\vartheta^*)$	− 28.28	$e_2(\pi_\varphi^*)$
− 28.95	$e_3(\pi_\varphi^*)$	− 29.08	$e_3(\pi_\varphi^* > \pi_\vartheta^*)$
− 30.22	$e_1(\pi_\vartheta^*)$	− 30.24	$e_1(\pi_\vartheta^*)$
− 52.87	$e_3(d > \sigma)$	− 49.05	$e_3(d > \sigma)$
− 58.05	$e_2(d > \sigma)$	− 53.89	$e_2(d > \sigma)$
− 81.72	$a_1(d)$	− 73.91	$a_1(d)$
−104.07	$a_2(\pi_\varphi)$	−104.07	$a_2(\pi_\varphi)$
−105.23	$b_2(\sigma > \pi_\vartheta)$	−104.81	$e_2(\sigma > d, \pi)$
−106.77	$e_3(\pi_\vartheta)$	−104.83	$b_2(\sigma > \pi_\vartheta)$
−107.66	$e_2(\sigma > \pi, d)$	−106.46	$e_3(\pi_\vartheta > \pi_\varphi)$
−108.51	$e_1(\pi_\varphi > \sigma)$	−108.20	$e_1(\pi_\varphi > \sigma)$
−111.18	$b_1(\pi_\varphi)$	−110.66	$e_3(\sigma > \pi_\varphi, d)$
⋮		⋮	
−113.64	$e_3(\sigma > d, \pi)$	⋮	
⋮		⋮	
−137.05	$e_1(\sigma, \pi_\varphi, \pi_\vartheta)$	−136.32	$e_1(\sigma, \pi_\varphi, \pi_\vartheta)$
⋮		⋮	
−158.37	$a_1(\sigma > s)$	−155.38	$a_1(\sigma > s)$

Table 2. *Populations of orthogonalized atomic and ligand orbitals*

Type of MO	$n(s)$	$n(d)$	$n(\sigma)$	$n(\pi_\vartheta)$	$n(\pi_\varphi)$	$n(\pi_\vartheta^*)$	$n(\pi_\varphi^*)$
$Mo(CN)_8^{3-}$							
$a_1(d)$	0.003	0.863	0.000	0.097	0.000	0.037	0.000
$e_2(d > \sigma)$	0.000	0.540	0.396	0.003	0.013	0.009	0.039
$e_3(d > \sigma)$	0.000	0.539	0.408	0.003	0.004	0.019	0.025
$Mo(CN)_8^{4-}$							
$a_1(d)$	0.003	0.883	0.000	0.069	0.000	0.045	0.000
$e_2(d > \sigma)$	0.000	0.609	0.316	0.003	0.013	0.011	0.048
$e_3(d > \sigma)$	0.000	0.599	0.337	0.003	0.004	0.025	0.032

The ordering of the three "*d*" levels is qualitatively the same as that what follows from the crystal field theory:

$$a_1(d_{z^2}) < e_2(d_{x^2-y^2} > \sigma, d_{xy} > \sigma) < e_3(d_{xz} > \sigma, d_{yz} > \sigma) .$$

The overall splitting increases with the oxidation degree of the molybdenum atom being equal to 24.9 kK for Mo(IV) and 28.9 kK for Mo(V). Such a strong dependence seems to prove that Perumareddi's *et al.* assumption of independence of this splitting from the oxidation degree was rather unrealistic.

It is interesting to compare the splitting of "d" levels in $\mathrm{Mo(CN)_8^{4-}}$, obtained in the present SCCC MO calculations, with that predicted by the crystal field theory for a twisted cube model [28] and a flattened antiprism [24]. One finds (in kK):

	$E(e_2)-E(a_1)$	$E(e_3)-E(e_2)$
SCCC MO method	20.0	4.9
CFT (twisted cube model)	12.3	12.3
CFT (flattened antiprism)	22.4	9.9

It follows from this comparison that the formalism of the crystal field theory can be also used to antiprismatic complexes of a D_{4d} symmetry yielding useful information, provided a realistic model of the complex is used.

4. Interpretation of the Absorption Spectrum of $\mathrm{Mo(CN)_8^{3-}}$ Ions

The calculated electronic transition energies and the absorption spectrum observed in aqueous solution are compared in Table 3 and in Fig. 3. The calculated transition energies do not include corrections for interelectronic repulsion. Owing to the large delocalization of the electrons in question the correction should not exceed 2–3 kK. However, because of a near degeneracy of some excited states in this approximation configuration interaction may play a significant role. We are not able at present to follow the CI effect quantitatively. Qualitatively, however, the effect is easy to follow as two mixing levels push always one each other apart. Such a qualitative effect of CI (of an order 2–3 kK) is indicated in Table 3 by inequality signs in column 6 and by horizontal arrows in Fig. 3.

Table 3. *Interpretation of the absorption spectrum of* $\mathrm{Mo(CN)_8^{3-}}$

Experiment [28]		Configurational excitation		Excited state	Character and polarization	ΔE_{calc}
ΔE (kK)	$\varepsilon_{\max}^{\mathrm{corr}}$					
25.8	1560	$a_2(\pi_\varphi)\rightarrow a_1(d)$		$^2A_2$	forb. CT	22.3
		$a_1(d)\rightarrow e_2(d>\sigma)$	mixed with $e_2(\sigma>\pi, d)\rightarrow a_1(d)$	$^2E_2$	forb. dd	<23.2
		$b_2(\sigma>\pi_\vartheta)\rightarrow a_1(d)$		$^2B_2$	$\parallel$, CT	23.5
		$e_3(\pi_\vartheta)\rightarrow a_1(d)$	mixed with $a_1(d)\rightarrow e_3(d>\sigma)$	$^2E_3$	forb. CT	<25.1
		$e_2(\sigma>\pi, d)\rightarrow a_1(d)$	mixed with $a_1(d)\rightarrow e_2(d>\sigma)$	$^2E_2$	forb. CT	25.9
		$e_1(\pi_\varphi>\sigma)\rightarrow a_1(d)$		$^2E_1$	$\perp$, CT	26.8
32.2	600	$a_1(d)\rightarrow e_3(d>\sigma)$	mixed with $e_3(\sigma>d)\rightarrow a_1(d)$	$^2E_3$	forb. dd	28.9
		$b_1(\pi_\varphi)\rightarrow a_1(d)$		$^2B_1$	forb. CT	29.5
		$e_2(\pi_\vartheta)\rightarrow a_1(d)$	mixed with $e_2(\sigma>\pi, d)\rightarrow a_1(d)$	$^2E_2$	forb. CT	>29.5
		$e_3(\sigma>d, \pi)\rightarrow a_1(d)$	mixed with $a_1(d)\rightarrow e_3(d>\sigma)$	$^2E_3$	forb. CT	>31.9
37.4 39.5	2000 2000	$e_1(\pi_\vartheta)\rightarrow a_1(d)$	mixed with $e_3(\pi_\vartheta)\rightarrow e_2(d>\sigma)$ etc.	$^2E_1$	$\perp$, CT	<41.2
gap		$a_2(\pi_\varphi)\rightarrow e_2(d>\sigma)$	mixed with $b_2(\sigma>\pi_\vartheta)\rightarrow e_2(d>\sigma)$	$^2E_2$	forb. CT	<45.5
		vice versa		$^2E_2$	forb. CT	>46.7
50.0	—	$e_3(\pi_\vartheta)\rightarrow e_2(d>\sigma)$	mixed with $e_1(\pi_\varphi>\sigma)\rightarrow e_2(d>\sigma)$	$^2E_1$	$\perp$, CT	>48.3
		$e_2(\sigma>\pi, d)\rightarrow e_2(d>\sigma)$		$^2B_2$	$\parallel$, CT	49.1

It is also difficult to estimate the oscillator strengths theoretically. Visualizing the theoretical spectrum in Fig. 3 we have made the following assumption which seems to be reasonable: maxima of allowed "charge-transfer" bands are assumed to be 10 times higher than those of forbidden ones and 100 times higher than those of "$d-d$" transitions. The terminology "charge-transfer" bands and "$d-d$" bands is here used to stress the principle character of the transition from one molecular orbital to another one.

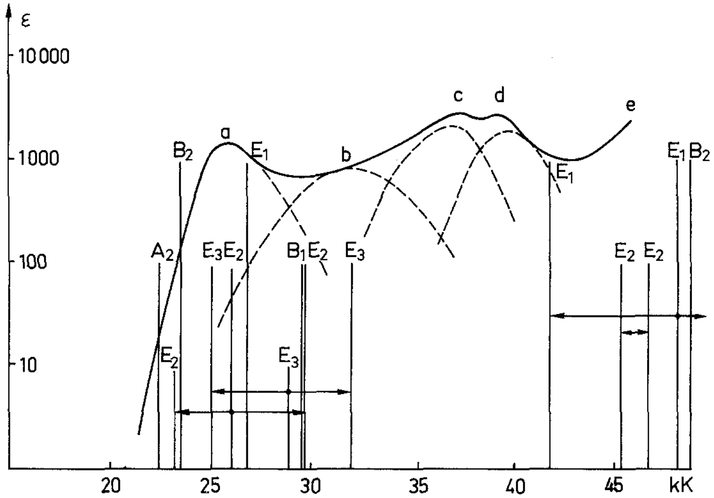

Fig. 3. Absorption spectrum of an aqueous solution of Mo(CN)$_8^{3-}$, redrawn from Ref. [37]

According to König [28] the spectrum of Mo(CN)$_8^{3-}$ cannot be interpreted in terms of the crystal field theory. Indeed, we see from Fig. 3 that the two "$d-d$" transitions $^2A_1 \rightarrow {}^2E_2$ and $^2A_1 \rightarrow {}^2E_3$ are covered by "charge-transfer" bands.

It follows from Fig. 3 that the reproduction of the observed spectrum is very satisfactory in spite of the important fact that none of the empirical parameters has been optimized in order to fit the spectrum.

Band a at 25.8 kK ($\varepsilon_{\max}^{\text{corr}} = 1560$) is asymmetric. A glance at the spectrum of the isomorphous W(CN)$_8^{3-}$ ion in water solution (Fig. 4 taken from Ref. [37]) seems to indicate that a double peak cannot be excluded. Theoretically two allowed "charge-transfer" transitions lie in this region, with different polarizations: $^2A_1 \rightarrow {}^2B_2$ with a $\parallel$ polarization and $^2A_1 \rightarrow {}^2E_1$ with a $\perp$ polarization. They correspond to excitations $b_2(\sigma > \pi_\vartheta) \rightarrow a_1(d)$ and $e_1(\pi_\varphi > \sigma) \rightarrow a_1(d)$ respectively. However, we cannot exclude the second transition to correspond to the band b.

Band b is very flat and broad (Figs. 3 and 4), with $\Delta E = 32.2$ kK and $\varepsilon_{\max}^{\text{corr}} = 600$ in the case of Mo(CN)$_8^{3-}$. We expect that three closely lying "charge-transfer" forbidden transitions are responsible for this broad band: $^2A_1 \rightarrow {}^2B_1$ at 29.5 kK, $^2A_1 \rightarrow {}^2E_2$ at 29.5 kK and $^2A_1 \rightarrow {}^2E_3$ at 31.9 kK. The appropriate configuration excitation is given in column 3 of Table 3. The flatness and broadness of the observed band seems to support this view.

Bands c and d at 37.4 kK and 39.5 kK with both $\varepsilon_{\max}^{\text{corr}}$ equal to 2000 are assigned as the $^2A_1 \rightarrow {}^2E_1$ transition of a $\perp$ polarization. We see two possible explanations for the splitting of the band which may be related one with each other. The excited state is degenerate and strongly antibonding. Thus a sufficiently strong Jahn-Teller effect might be expected (for example with a twisting towards the D_{2d} model). On the other hand, the difference in transition energies $39.5 - 37.4 = 2.1$ *kK* is approximately equal to the vibration excitation energy of CN^- stretching vibrations.

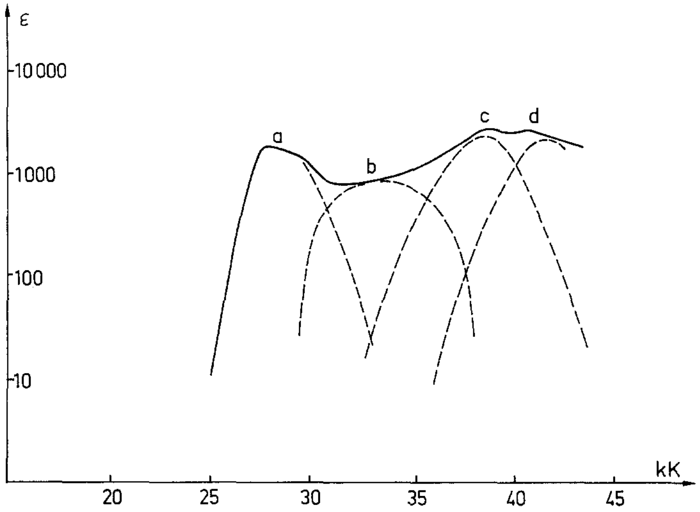

Fig. 4. Absorption spectrum of an aqueous solution of $W(CN)_8^{3-}$, redrawn from Ref. [37]

The nature of the *e* band seems to be complex. Two calculated transitions lie at 48.2 *kK* and 50.0 *kK* and several other at slightly higher energies.

There is no deep gap between the bands *d* and *e*. According to the SCCC MO calculations two forbidden transitions fall into this region, at 45.5 *kK* and 46.7 *kK*.

5. Interpretation of the Absorption Spectrum of the Jakób Compound

The calculated transition energies in a $Mo(CN)_8^{4-}$ ion of a D_{4d} symmetry are compared in Fig. 5 and Table 4 with the observed spectrum of an aqueous solution of the Jakób compound. Notation and comments are the same as in the preceding section. "Theoretical" intensities in Fig. 5 are drawn according to the following convention: ε_{max} of a double "$d-d$" excitation is 10 times smaller than of a "$d-d$" single excitation, 100 times smaller than that of a forbidden CT transition and 1000 times smaller than that of an allowed CT band.

One can see from Fig. 5 that two results of the SCCC MO calculations are gratifying: the two "$d-d$" bands *a* and *b* and the first strongly allowed band *e* are reproduced interestingly well.

However, interpretation of the bands *c* and *d* is not satisfactory. One possibility lies in double excitations $a_1(d)^2 \to e_2(d > \sigma)^2$, that is ${}^1A_1 \to {}^1B_1$ and ${}^1A_1 \to {}^1B_2$. The estimated transition energies (with a correction for repulsion of the "d" electrons) are about 37–38 *kK* (Fig. 5). Charge transfer states of the ${}^1B_1$ and ${}^1B_2$

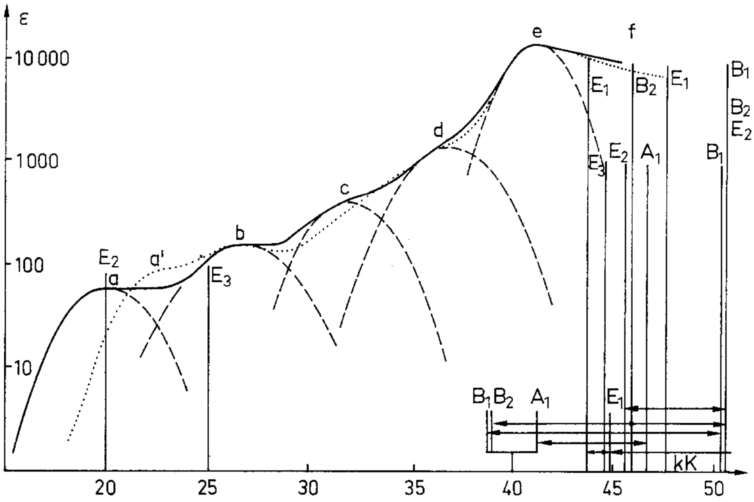

Fig. 5. Absorption spectrum of an aqueous solution of the Jakób compound, redrawn from Ref. [23] (solid line; in 2.6 *n* NH_3). The dotted line shows the spectrum of an aqueous solution of $K_4\,Mo(CN)_8$, redrawn from Ref. [37]

Table 4. *Interpretation of the absorption spectrum of the* $Mo(CN)_8^{4-}$ *unit in the Jakób compound*

Experiment [21] $\Delta E(kK)$	$\varepsilon_{\max}^{\text{corr}}$	Configurational excitation	Excited state	Character and polarization	ΔE_{calc} (kK)
20.9	58	$a_1(d)\rightarrow e_2(d>\sigma)$	$^1E_2$	forb. dd	20.0
27.3	145	$a_1(d)\rightarrow e_3(d>\sigma)$	$^1E_3$	forb. dd	24.9
32.6	365	$a_1(d)^2\rightarrow e_2(d>\sigma)^2$ mixed with $a_1(d)\rightarrow b_2(\pi_\vartheta^*)$?	$^1B_2$?	$dd+\text{CT}(\Vert)$?	<38.0
37.5	1260	$a_1(d)^2\rightarrow e_2(d>\sigma)^2$ mixed with $a_1(d)\rightarrow b_1(\pi_\varphi^*)$?	$^1B_1$?	$dd+$ forb. CT?	<38.0
		$a_1(d)^2\rightarrow e_2(d>\sigma)\,e_3(d>\sigma)$ with almost 0-th order CI with $a_1(d)\rightarrow e_1(\pi_\vartheta^*)$?	$^1E_1$?	$dd+\text{CT}(\perp)$?	<44.0
41.6	12940	$a_1(d)\rightarrow e_1(\pi_\vartheta^*)$ mixed with $a_1(d)^2\rightarrow e_2(d>\sigma)$. $e_3(d>\sigma)$ and $a_1(d)\rightarrow e_1(\pi_\varphi^*)$	$^1E_1$	$\perp$, CT	43.7
		$a_1(d)\rightarrow b_2(\pi_\vartheta^*)$	$^1B_2$	$\Vert$, CT	45.9

species lie at slightly higher energies (Fig. 5). They certainly will push the other two states down, causing simultaneously a gain in oscillator strengths.

Let us add a comment: all the calculated "charge-transfer" transitions lie very close one to each other. Thus a configuration interaction and a proper account of ligand-ligand interactions is likely to push them apart. This would broaden the spectrum in the CT region and could lead to another explanation of the irregular position of bands *c* and *d*.

Appendix

Symmetry Orbitals in Complexes of D_{4d} Symmetry

Let us denote the σ, π_ϑ, π_ϑ^*, π_φ, and π_φ^*-type orbitals of the k-th ligand ($k=1,2,\ldots,8$) simply by σ_k, ϑ_k, ϑ_k^*, φ_k, and φ_k^* respectively. Let us also introduce two types of column vectors,

$$\mu = \begin{pmatrix} \mu_1 \\ \mu_2 \\ \vdots \\ \mu_8 \end{pmatrix} \quad \text{and} \quad (\mu_1 | \nu) = \begin{pmatrix} \langle \mu_1 | \nu_1 \rangle \\ \langle \mu_1 | \nu_2 \rangle \\ \vdots \\ \langle \mu_1 | \nu_8 \rangle \end{pmatrix}$$

where μ, ν stand for $\sigma, \vartheta, \vartheta^*, \varphi$ or φ^*. Finally, let us introduce the following 8 row vectors:

$$\begin{array}{l}
A = (1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1) \\
B = (1 \;\; 1 \;\; 1 \;\; 1 \;\; -1 \;\; -1 \;\; -1 \;\; -1) \\
C = (1 \;\; 1 \;\; -1 \;\; -1 \;\; 0 \;\; \sqrt{2} \;\; 0 \;\; -\sqrt{2}) \\
D = (1 \;\; 1 \;\; -1 \;\; -1 \;\; 0 \;\; -\sqrt{2} \;\; 0 \;\; \sqrt{2}) \\
E = (1 \;\; -1 \;\; -1 \;\; 1 \;\; \sqrt{2} \;\; 0 \;\; -\sqrt{2} \;\; 0) \\
F = (1 \;\; -1 \;\; -1 \;\; 1 \;\; -\sqrt{2} \;\; 0 \;\; \sqrt{2} \;\; 0) \\
G = (1 \;\; -1 \;\; 1 \;\; -1 \;\; 0 \;\; 0 \;\; 0 \;\; 0) \\
H = (0 \;\; 0 \;\; 0 \;\; 0 \;\; 1 \;\; -1 \;\; 1 \;\; -1)
\end{array}$$

We can then write the symmetry orbitals in the following short form:

Representation a_1 (or γ_1),

$$s,\ d_{z^2},\ \Sigma_1 = 8^{-\frac{1}{2}} N(\Sigma_1) A\sigma,\ \Theta_1 = 8^{-\frac{1}{2}} N(\Theta_1) B\vartheta,\ \Theta_1^* = 8^{-\frac{1}{2}} N(\Theta_1^*) B\vartheta^* ;$$

Representation a_2 (or γ_2),

$$\Phi_2 = 8^{-\frac{1}{2}} N(\Phi_2) A\varphi,\ \Phi_2^* = 8^{-\frac{1}{2}} N(\Phi_2^*) A\varphi^* ;$$

Representation b_1 (or γ_3),

$$\Phi_3 = 8^{-\frac{1}{2}} N(\Phi_3) B\varphi,\ \Phi_3^* = 8^{-\frac{1}{2}} N(\Phi_3^*) B\varphi^* ;$$

Representation b_2 (or γ_4),

$$p_z,\ \Sigma_4 = 8^{-\frac{1}{2}} N(\Sigma_4) B\sigma,\ \Theta_4 = 8^{-\frac{1}{2}} N(\Theta_4) A\vartheta,\ \Theta_4^* = 8^{-\frac{1}{2}} N(\Theta_4^*) A\vartheta^* ;$$

Representation e_1 (or γ_5), component transforming like x,

$$p_x,\ \Sigma_5 = 8^{-\frac{1}{2}} N(\Sigma_5) C\sigma,\ \Theta_5 = 8^{-\frac{1}{2}} N(\Theta_5) D\vartheta,\ \Theta_5^* = 8^{-\frac{1}{2}} N(\Theta_5^*) D\vartheta^* ,$$

$$\Phi_5 = 8^{-\frac{1}{2}} N(\Phi_5) E\varphi,\ \Phi_5^* = 8^{-\frac{1}{2}} N(\Phi_5^*) E\varphi^* ;$$

Representation e_2 (or γ_6), component transforming like xy,

$$d_{xy},\ \Sigma_6 = \tfrac{1}{2} N(\Sigma_6) G\sigma,\ \Theta_6 = \tfrac{1}{2} N(\Theta_6) G\vartheta,\ \Theta_6^* = \tfrac{1}{2} N(\Theta_6^*) G\vartheta^* ,$$

$$\Phi_6 = \tfrac{1}{2} N(\Phi_6) H\varphi,\ \Phi_6^* = \tfrac{1}{2} N(\Phi_6^*) H\varphi^* ;$$

Representation e_3 (or γ_7), component transforming like xz,

$$d_{xz},\ \Sigma_7 = 8^{-\frac{1}{2}} N(\Sigma_7) D\sigma,\ \Theta_7 = 8^{-\frac{1}{2}} N(\Theta_7) C\vartheta,\ \Theta_7^* = 8^{-\frac{1}{2}} N(\Theta_7^*) C\vartheta^*,$$

$$\Phi_7 = 8^{-\frac{1}{2}} N(\Phi_7) F\varphi,\ \Phi_7^* = 8^{-\frac{1}{2}} N(\Phi_7^*) F\varphi^*,$$

where $N(\Sigma_1)$, $N(\Theta_1)$, etc., are renormalization coefficients. If overlap integrals between different ligand orbitals are neglected, then all N's are equal 1. All the ligand symmetry orbitals have the general form $\Omega = aN(\Omega)Q\mu$, where $a = 8^{-\frac{1}{2}}$ or $\frac{1}{2}$ and Q is one of the matrices $A, B, \ldots, H$. One can check that except for $N(\Phi_6)$ and $N(\Phi_6^*)$ the following reduction formula is valid: $N(\Omega) = [Q(\mu_1|\mu)]^{-\frac{1}{2}}$. For the remaining two renormalization coefficients one gets: $N(\Phi_6) = [G(\varphi_1|\varphi)]^{-\frac{1}{2}}$, $N(\Phi_6^*) = [G(\varphi_1^*|\varphi^*)]^{-\frac{1}{2}}$.

Reduction Formulae for Ligand-Ligand Group Overlap Integrals

Using the same notation one can find what follows:

$$(\Sigma_1|\Theta_1) = N(\Sigma_1)\,N(\Theta_1)\,B(\sigma_1|\vartheta), \quad (\Theta_1|\Theta_1^*) = N(\Theta_1)\,N(\Theta_1^*)\,B(\vartheta_1|\vartheta^*),$$

$$(\Phi_2|\Phi_2^*) = N(\Phi_2)\,N(\Phi_2^*)\,A(\varphi_1|\varphi^*), \quad (\Phi_3|\Phi_3^*) = N(\Phi_3)\,N(\Phi_3^*)\,B(\varphi_1|\varphi^*),$$

$$(\Sigma_4|\Theta_4) = N(\Sigma_4)\,N(\Theta_4)\,A(\sigma_1|\vartheta), \quad (\Theta_4|\Theta_4^*) = N(\Theta_4)\,N(\Theta_4^*)\,A(\vartheta_1|\vartheta^*),$$

$$(\Sigma_5|\Theta_5) = N(\Sigma_5)\,N(\Theta_5)\,D(\sigma_1|\vartheta), \quad (\Phi_5|\Phi_5^*) = N(\Phi_5)\,N(\Phi_5^*)\,E(\varphi_1|\varphi^*),$$

$$(\Sigma_5|\Phi_5) = N(\Sigma_5)\,N(\Phi_5)\,E(\sigma_1|\varphi), \quad (\Theta_5|\Theta_5^*) = N(\Theta_5)\,N(\Theta_5^*)\,D(\vartheta_1|\vartheta^*),$$

$$(\Theta_5|\Phi_5) = N(\Theta_5)\,N(\Phi_5)\,E(\vartheta_1|\varphi), \quad (\Sigma_6|\Theta_6) = N(\Sigma_6)\,N(\Theta_6)\,G(\sigma_1|\vartheta),$$

$$(\Sigma_6|\Phi_6) = N(\Sigma_6)\,N(\Phi_6)\,H(\sigma_1|\varphi), \quad (\Theta_6|\Theta_6^*) = N(\Theta_6)\,N(\Theta_6^*)\,G(\vartheta_1|\vartheta^*),$$

$$(\Phi_6|\Phi_6^*) = N(\Phi_6)\,N(\Phi_6^*)\,G(\varphi_1|\varphi^*), \quad (\Theta_6|\Phi_6) = N(\Theta_6)\,N(\Phi_6)\,H(\vartheta_1|\varphi),$$

$$(\Sigma_7|\Theta_7) = N(\Sigma_7)\,N(\Theta_7)\,E(\sigma_1|\vartheta), \quad (\Sigma_7|\Phi_7) = N(\Sigma_7)\,N(\Phi_7)\,F(\sigma_1|\varphi),$$

$$(\Theta_7|\Theta_7^*) = N(\Theta_7)\,N(\Theta_7^*)\,E(\vartheta_1|\vartheta), \quad (\Phi_7|\Phi_7^*) = N(\Phi_7)\,N(\Phi_7^*)\,F(\varphi_1|\varphi^*),$$

$$(\Theta_7|\Phi_7) = N(\Theta_7)\,N(\Phi_7)\,F(\vartheta_1|\varphi).$$

Reduction Formulae for Metal-Ligand Group Overlap Integrals

$$(s|\Sigma_1) = \sqrt{8}\,N(\Sigma_1)S_{\sigma s}, \quad (s|\Theta_1) = 0,$$

$$(d_{z^2}|\Sigma_1) = \tfrac{1}{2}\sqrt{8}\,N(\Sigma_1)\,(3\cos^2\vartheta - 1)S_{\sigma d}, \quad (d_{z^2}|\Theta_1) = \sqrt{6}\,N(\Theta_1)\sin 2\vartheta S_{\pi d},$$

$$(p_z|\Sigma_4) = \sqrt{8}\,N(\Sigma_4)\cos\vartheta S_{\sigma p}, \quad (p_z|\Theta_4) = \sqrt{8}\,N(\Theta_4)\sin\vartheta S_{\pi p},$$

$$(p_x|\Sigma_5) = -2N(\Sigma_5)\sin\vartheta S_{\sigma p}, \quad (p_x|\Theta_5) = 2N(\Theta_5)\cos\vartheta S_{\pi p},$$

$$(p_x|\Phi_5) = -2N(\Phi_5)S_{\pi p}, \quad (d_{xy}|\Sigma_6) = -\sqrt{3}\,N(\Sigma_6)\sin^2\vartheta S_{\sigma d},$$

$$(d_{xy}|\Theta_6) = N(\Theta_6)\sin 2\vartheta S_{\pi d}, \quad (d_{xy}|\Phi_6) = -2N(\Phi_6)\sin\vartheta S_{\pi d},$$

$$(d_{xz}|\Sigma_7) = -\sqrt{3}\,N(\Sigma_7)\sin 2\vartheta S_{\sigma d}, \quad (d_{xz}|\Theta_7) = 2N(\Theta_7)\cos 2\vartheta S_{\pi d},$$

$$(d_{xz}|\Phi_7) = -2N(\Phi_7)\cos\vartheta S_{\pi d},$$

where $S_{\sigma s}$, $S_{\sigma p}$, $S_{\sigma d}$, $S_{\pi p}$, and $S_{\pi d}$ are standard overlap integrals defined in Fig. 6.

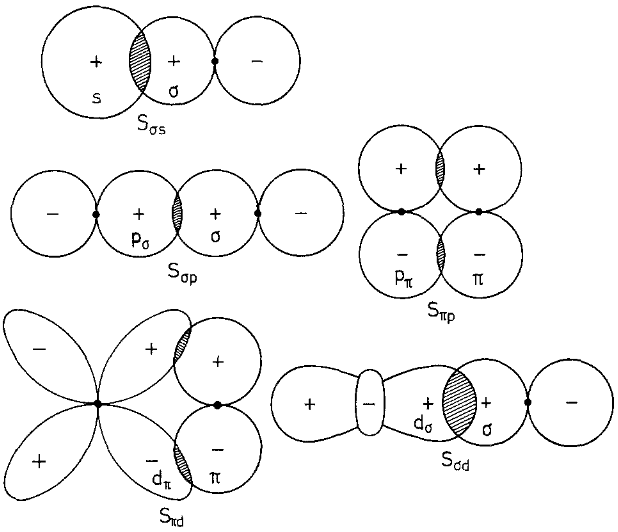

Fig. 6

The authors are grateful to Prof. W. Jakób, Dr. Z. Stasicka and Dr. A. Samotus for many interesting discussions, to Prof. J. Chojnacki for providing us with new X-ray results before publication and to Dr. A. J. Sadlej for a help in dealing with the computer.

References

1. Ballhausen, C. J., and H. B. Gray: Molecular orbital theory. New York: Benjamin 1965.
2. Basch, H., and H. B. Gray: Theoret. chim. Acta (Berl.) **4**, 367 (1966).
3. — A. Viste, and H. B. Gray: J. chem. Physics **44**, 10 (1966).
4. Basu, M., and S. Basu: J. inorg. nuclear Chem. **30**, 467 (1968).
5. Bertoluzza, A., V. Carassiti, and A. M. Marinangeli: Ann. di Chimica **50**, 645 (1960).
6. Bishop, D. M., M. Randic, and J. R. Morton: J. chem. Physics **45**, 1880 (1966).
7. Duffey, G. H.: J. chem. Physics **18**, 746 (1950).
8. Fenske, R. F., K. G. Caulton, D. D. Radtke, and C. C. Sweeney: Inorg. Chemistry **5**, 951, 960 (1966).
9. Fisher-Hjalmars, I.: Theoret. chim. Acta (Berl.) **4**, 332 (1966).
10. Garvey, B. R.: Inorg. Chemistry **5**, 476 (1966).
11. Gliemann, G.: Theoret. chim. Acta (Berl.) **1**, 14 (1962).
12. Golding, R. M., and A. Carrington: Molecular Physics **5**, 377 (1962).
13. Gołębiewski, A.: In: Theory and structure of complex compounds, ed. by Jezowska-Trzebiatowska, Wroclaw 1962.
14. Griffith, J. S., and L. E. Orgel: Quart. Review (London) **11**, 381 (1957).
15. Griffiths, J. H. E., J. Owen, and I. M. Ward: Proc. Roy. Soc. (London) A **219**, 526 (1953).
16. Hayes, R. G.: J. chem. Physics **44**, 2210 (1966).
17. Hoard, J. L., and H. H. Nordsieck: J. Amer. chem. Soc. **61**, 2853 (1939).
18. — J. V. Silverton, G. L. Glen, and E. Willstadter: Proc. 7 ICCC, Stockholm 1962.
19. — — Inorg. Chemistry **2**, 235 (1963).
20. Ingraham, L. L.: Acta Chem. Scandinavica **20**, 283 (1966).
21. Jakób, W., and Z. Jakób: Ann. Soc. Chim. Polonorum **36**, 601 (1962).
22. — A. Samotus, and Z. Stasicka: Ann. Soc. Chim. Polonorum **36**, 611 (1962).
23. —, and Z. Stasicka: Ph. D. thesis, Jagiellonian University 1963.
24. — A. Samotus, Z. Stasicka, and A. Gołębiewski: Z. Naturforschung **21** b, 819 (1966).
25. Jørgensen, C. K.: Absorption spectra and chemical bonding in complexes. Oxford-London-New York-Paris: Pergamon Press 1962.

26. Kepert, D. L.: J. chem. Soc. (London) **1965**, 4736.
27. — Theoret. chim. Acta (Berl.) **11**, 51 (1968).
28. König, E.: Theoret. chim. Acta (Berl.) **1**, 23 (1962).
29. Löwdin, P.-O.: J. chem. Physics **18**, 365 (1950).
30. Manoharan, P. T., and H. B. Gray: J. Amer. chem. Soc. **87**, 3340 (1965).
31. — — Inorg. Chemistry **5**, 823 (1966).
32. Moore, Ch. E.: Atomic energy levels. Natl. Bur. Standards (U.S.A.) Circ. No. 467, vol. III.
33. Muetterties, E. I.: Inorg. Chemistry **4**, 769 (1965).
34. Mulliken, R. S.: J. chem. Physics **23**, 1833, 1841 (1955).
35. Orgel, L. E.: J. inorg. nuclear Chemistry **14**, 136 (1960).
36. Parish, R. V.: Spectrochim. Acta **22**, 1191 (1966).
37. Perumareddi, J. R., A. D. Liehr, and A. W. Adamson: J. Amer. chem. Soc. **85**, 249 (1963).
38. Racah, G.: J. chem. Physics **11**, 214 (1943).
39. Randič, M.: J. chem. Physics **36**, 2094 (1962).
40. Rico, F. R.: Anales de la Real Soc. Espanola de Fisica y Quimica, A **61**, 103 (1965).
41. Roothaan, C. C. J.: Physic. Rev. **133**, A 1263 (1964).
42. Schläfer, H. L., and F. Wasgestian: Cited in Ref. [9].
43. Stamreich, H., u. O. Sala: Z. Elektrochemie **64**, 741 (1960); **65**, 149 (1961).
44. Viste, A., and. H. B. Gray: Inorg. Chemistry **3**, 1113 (1964).
45. Weissman, S. I., and M. Cohn: J. chem. Physics **27**, 1440 (1957).
46. —, and C. S. Garner: J. Amer. chem. Soc. **78**, 1072 (1956).
47. Wolfsberg, M., and L. Heimholz: J. chem. Physics **20**, 837 (1952).
48. Yeranos, W. A.: Inorg. Chemistry **5**, 2070 (1966).

Doc. Dr. Alojzy Gołębiewski
Department of Theoretical Chemistry
Jagiellonian University
ul. Krupnicza 41, Cracow, Poland