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Ab Initio Study of Progressive Ligand Substitution in Octahedral Transition-Metal Complexes

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Near-Hartree–Fock-limit calculations are presented for the two isomers of the tetracyanodihydroxocobaltate(III) anion. An analysis of the ground-state wave functions as well as the ΔSCF spectra does confirm the ligand field description of their electronic structure. The calculated term splittings within the t^5e^1 configuration can quite accurately be described by means of a single set of theoretical ligand field parameters. The relevance of the holohedron concept is maintained at the Hartree–Fock level of approximation, as shown by the near-degeneracy of certain orbital and state levels in the C_{2v} cis complex. Evidence in favor of the ligand additivity postulate can also be found from Mulliken population analysis and from total density difference plots. The previously given rationalization of ligand field photosubstitutions is in line with the present results.

I. Introduction

The effect of ligand substitution on the electronic structure of transition-metal complexes can readily be discussed in the framework of ligand field theory. More specifically, if one assumes the perturbation potential to be additive in the individual ligand contributions (as in the angular-overlap model for instance), substitution simply corresponds to changing one or more terms in the summation, describing the ligand field Hamiltonian. The transferability of these perturbations from one complex to another allows the description of related complexes in terms of a limited set of ligand field parameters.[1] In this way, the spectral data (band splittings and band shifts) as well as the (photo)chemical behavior of transition-metal complexes can be rationalized quite satisfactorily at the semiempirical level.[2,3]

In a previous paper,[4] we described an ab initio Hartree–Fock comparison of $Co(CN)_6^{3-}$ and $Co(CN)_5(OH)^{3-}$ in order to find out to what extent the physical assumptions of ligand field theory are justified. One of our results was that the inert ligand–metal bonds remain indeed essentially unaffected by the substitution process, thereby lending support for the ligand field idea of additive and transferable perturbations. It is the purpose of the present paper to extend this investigation and to present a comparison of the nonsubstituted hexacyano Co(III) complex with the corresponding pentacyano–hydroxo and the two (cis and trans) tetracyano–dihydroxo Co(III) complexes.

II. Method of Calculation

Roothaan's RHF formalism was used throughout, both for closed and for open shells,[5] with the Symol program, developed by Nieuwpoort's group in Groningen.[6] A rather large basis set should guarantee (a near-Hartree–Fock-limit) high-quality results: for the metal atom, we used a (15s,11p,6d/11s,8p,4d) basis set, for the first row ligand atoms a (9s,5p/5s,3p) basis set, and for H a (4s/3s) basis set. The orbital exponents, the metal–ligand balance, and the contraction scheme have been discussed in previous papers.[7-9] Experimental bond lengths are available[10,11] for the hexacyano complex: R(Co–C) = 1.89 Å and R(C–N) = 1.15 Å. For the substituted complexes, the Co–C and C–N distances were taken to be identical with those in the hexacyano complex. The Co–O distance was estimated[4] to be 1.85 Å and the O–H distance to be 0.97 Å.

III. Ground-State Analysis

The general pattern describing the two disubstituted complexes is similar to that of the nonsubstituted and the monosubstituted compound:[4] all molecular orbitals preserve a predominant character (Co, CN, or OH); the metal d orbitals are situated within the energetic range of the 4σ (CN) orbitals; the π ligand orbitals are more destabilized than the σ ligand orbitals; the upper levels of the substituted complexes are characterized by an (artificially) positive orbital energy. Introduction of the positive counterions would shift all energy levels more or less uniformly downward.[12,13]

An interesting feature of the relevant correlation diagram is the evolution of the metal dπ orbitals (see Figure 1). The octahedral 3-fold degenerate t_{2g} orbitals are split in two (D_{4h}, C_{4v}) or three (C_{2v}) energy levels. Actually, in C_{2v}, d_{xz} and d_{yz} are very nearly degenerate ($\Delta\eta$ = 417 cm^{-1}, where η is the orbital energy), suggesting an effectively higher symmetry. In additive ligand field theory, both orbitals are strictly degenerate, and the effective symmetry of the cis complex is also D_{4h}. Indeed, gerade orbitals (s, d, ...) experiencing perturbations, for example, on the $+x$ axis and on the $-x$ axis are sensitive only to the sum of these two perturbations; therefore, the x and y axes are equivalent, each one being the carrier of one CN^- and one OH^- ligand. The fact that this holohedral symmetry is very nearly realized in the Hartree–Fock calculation as well is another manifestation of the nearly pure metal 3d character of the relevant molecular orbitals.

Another prediction of ligand field theory is that the monosubstituted complex should have the same splitting (except for the sign) as the cis complex and half the splitting of the trans complex.[1-3] Therefore, the ratio of the d orbital splittings $\Delta\eta$ is expected to be 1:2:–1 for the monosubstituted, trans, and cis complexes, respectively. This prediction is confirmed rather nicely by the Hartree-Fock results of Figure 1, the actual numbers being 1953, 3775, and –1438 cm^{-1}. Yet, it is remarkable that the ligand field orbital energy differences and the SCF $\Delta\eta$ values have opposite signs in all substituted complexes. Indeed, in ligand field theory,[1-3] the OH^- ligand is generally classified as a strong π donor, and the xz, yz orbitals in the monosubstituted and trans disubstituted complexes are expected to be more destabilized than the xy orbital. The reason the Hartree–Fock calculations yield the opposite result is unclear; in the next section, however, it will be shown that the situation is again reversed at the state level.

Table I shows the results of a population analysis on the four complexes. The charge on the Co ion (formally +3) is seen to

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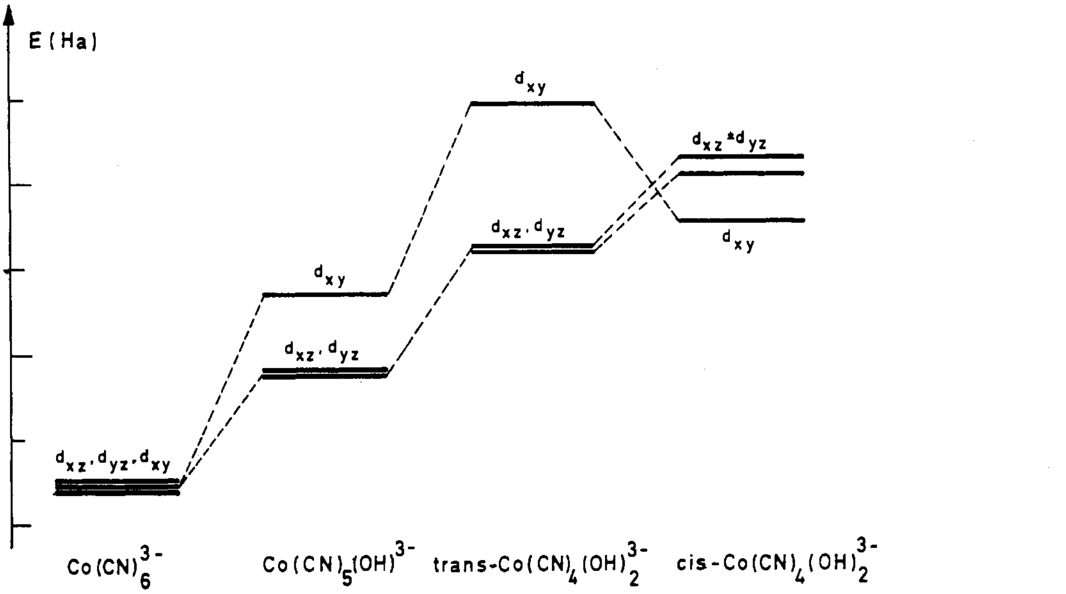

Figure 1. Hartree–Fock d orbital energy diagram (in hartrees for the individual ligands and the four complexes under consideration (all molecules in their ground states); the z axis is the hetero axis. For the cis complexes, xz and yz are acceptable orbitals only in the case of strict degeneracy; in the actual C_{2v} symmetry, the eigenorbitals are better described by $(1/2^{1/2})$ $(xz \pm yz)$.

Table I. Partial Results of a Mulliken Population Analysis, Showing the Most Relevant Orbital Populations and Atomic Charges in the Ground States of the Four Complexes

	$Co(CN)_6^{3-}$	$Co(CN)_5(OH)^{3-}$	*trans*-$Co(CN)_4(OH)_2^{3-}$	*cis*-$Co(CN)_4(OH)_2^{3-}$
$3d\pi$(Co)	5.72	5.73	5.73	5.73
$3d\sigma$(Cp)	1.63	1.37	1.16	1.16
q(Co)	+1.24	+1.59	+1.89	+1.83
$q(CN_{ax})$	−0.71	−0.75	−0.81	−0.80
$q(CN_{eq})$	−0.71	−0.76		−0.79
q(OH)		−0.80	−0.82	−0.81

Table II. Comparison of the Experimental Spectrum and the Lowest Calculated Energy Levels of the Two Disubstituted Complexes[a]

octahedral parentage	state (in D_{4h})	*trans*-$Co(CN)_4(OH)_2^{3-}$			*cis*-$Co(CN)_4(OH)_2^{3-}$		
		exptl	LF energy	SCF energy	exptl	LF energy	SCF energy
$^1A_{1g}$	$A_{1g}(xz^2yz^2xy^2)$	0	0	0	0	0	0
$^3T_{1g}$	$^3E_g^a(xz,yz \rightarrow z^2)$		11 762	3 253		19 722	11 593, 11 751
	$^3A_{2g}(xy \rightarrow x^2 - y^2)$		24 246	16 006		12 136	4679
$^3T_{2g}$	$^3B_{2g}(xy \rightarrow z^2)$		22 750	11 288		18 260	16 652
	$^3E_g^b(xz,yz \rightarrow x^2 - y^2)$		18 634	18 728		18 974	9475, 10 081
$^1T_{1g}$	$^1E_g^a(xz,yz \rightarrow z^2)$	20 600	19 754	14 437	25 700	27 714	22 799, 22 907
	$^1A_{2g}(xy \rightarrow x^2 - y^2)$		31 342	23 589	23 000	19 232	13 254
$^1T_{2g}$	$^1B_{2g}(xy \rightarrow z^2)$	30 000	33 430	28 485	31 000	28 940	
	$^1E_g^b(xz,yz \rightarrow x^2 - y^2)$		28 418	32 748	31 000	28 298	24 877, 25 450

[a] Both the first-order ligand field (LF) and the SCF energies are given in cm^{-1}. The levels of the cis complex are classified in the holohedron D_{4h} symmetry, rather than in the actual (C_{2v}) symmetry; therefore to each E level we associate two slightly different SCF energies, corresponding to $A_2 + B_2$ in C_{2v}.

increase from +1.24 in the hexacyano compound to +1.59 and +1.89 in the substituted complexes. This charge evolution is apparently not due to changes in the $d\pi$ population—which remains remarkably constant in all cases, corresponding to a more or less constant π back-donation of about 0.27 electron from Co^{3+} (d^6) to the ligand. The charge evolution of the metal is due almost entirely to the decreased σ donation from the ligands to the metal. Indeed, the hydroxyl ligand is a (slightly) weaker σ donor ($q \simeq -0.80$) than CN^- in $Co(CN)_6^{3-}$, where $q(CN^-) = -0.71$; moreover, OH^- preserves very nearly the same charge in all cases. In the cis complex, the cyanide charge is to a good approximation independent of the CN^- position (axial or equatorial). Also, the charges in the disubstituted cis and trans complexes are virtually identical, suggesting that the idea of additive bonds is not unrealistic. It is true, though, that the cyanide charge depends to some extent on the presence of OH^- (Table I); still, this fact hardly affects the overall description of the complex in terms of independent or "additive" bonds. Moreover, the general picture suggested by population analysis is confirmed by density difference plots, describing the bonding phenomenon in detail. The individual metal–ligand density difference plots are almost indistinguishable from one complex to another one or from axial to equatorial bonding site; plots of this type have been reported in a previous paper.[4]

The total energies of the two complexes are very similar: −1901.0570 hartrees for the trans complex and −1901.0539 hartrees for the cis complex. Therefore, at the SCF level, the present (large) basis set predicts the two complexes to be quite close in energy, with *trans*-$Co(CN)_4(OH)_2^{3-}$ ~2 kcal/mol more stable than *cis*-$Co(CN)_4(OH)_2^{3-}$. Experimentally, however, the cis complex appears to be the more stable isomer.[14,15] At room temperature, for instance, the trans complex is transformed into the cis complex. The failure of the calculation to reproduce the correct relative stabilities of the two isomers may be due to an

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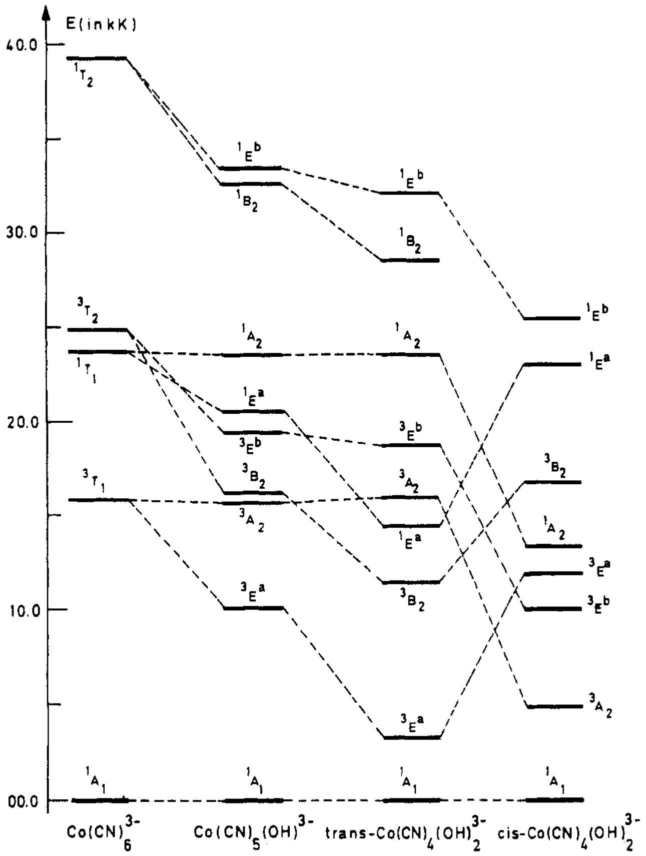

Figure 2. State correlation diagram of the Hartree–Fock levels for the four complexes under consideration in their t^6 and t^5e^1 configurations. The four ground states were arbitrarily set a equal energy. The energies for $Co(CN)_6{}^{3-}$ and $Co(CN)_5(OH)^{3-}$ were taken from ref 4. For the cis complex, the $^{1,3}E$ levels shown are the averages of the $^{1,3}A_2$ and $^{1,3}B_2$ levels obtained in C_{2v} symmetry. The parity subscript (g) has been dropped everywhere.

incorrect estimation of the metal–ligand bond lengths and to the absence of correlation energy.[16]

IV. Ligand Field Spectrum

Table II shows the position of the observed spectral bands[3,14,15,17] and the calculated energy of the lowest excited states, corresponding to the t^5e^1 configuration of octahedral parentage. The experimental data are very limited; to the extent that they are available, they can be rationalized by using first-order ligand field expressions.

At the Hartree–Fock level of approximation, the ab initio results cannot be expected to reproduce the experimental results quantitatively. It is more appropriate to compare the general pattern of the Hartree–Fock levels (also shown in Figure 2) with the predictions of ligand field theory.

(1) One of the more striking qualitative features is the splitting of the octahedral T_{1g} states into A_2 and E. Figure 2 shows how the splitting of the trans complex (both for singlet and triplet states) is approximately twice the splitting of the monosubstituted complex—in complete agreement with first-order ligand field theory. Even numerically, the SCF splitting and the ligand field splitting are quite comparable, although the overall position of the Hartree–Fock levels is definitely too low—a rather typical result.[4,12,13,18]

(2) The position of the A_2 levels (both $^1A_2$ and $^3A_2$) is remarkably constant in all cases except for the cis complex. Again, this result agrees with ligand field theory: the $A_1 \rightarrow A_2$ transition is essentially $xy \rightarrow x^2 - y^2$, and as such it takes place within the equatorial plane. Apparently the axial ligands do not affect the equatorial spectrochemical strength to any significant extent. To our knowledge, this simple ligand field conclusion had not received ab initio confirmation before.

Table III. Semiempirical Ligand Field Parameters (in cm^{-1}) Based on the Experimental Energies (Left-Hand Side)[3,16,18] and on a Fitting of the SCF Energies (Right-Hand Side) to the First-Order Ligand Field Expressions for the Four Complexes under Consideration

semiempirical LF params		Hartree–Fock LF params	
$10Dq(CN^-) = 3\sigma(CN^-) - 4\pi(CN^-)$	34890	$10Dq_{SCF}(CN^-)$	27266
B	448	B_{SCF}	997
C	3548	C_{SCF}	3560
$\Delta\sigma = \sigma(CN^-) - \sigma(OH^-)$	2540	$\Delta\sigma_{SCF}$	6063
$\Delta\pi = \pi(CN^-) - \pi(OH^-)$	−4150	$\Delta\pi_{SCF}$	−1647

(3) The holohedron effect in the cis complex was discussed already in the previous section. It also shows up very neatly in the excited states: Table II lists two closely spaced levels for each $^{1,3}E$ state. The fact that the energy splitting between the corresponding A_2 and B_2 states is so small (a few hundred cm^{-1}) suggests a negligible effect of 3d–4p mixing and of ligand–ligand interactions.

(4) All energy splittings (of $^{1,3}T_{1g}$ and $^{1,3}T_{2g}$) change sign in going from the cis to the trans complex. Again, this agrees with additive ligand field theory, where the splitting is traced back to the σ and π bond strength of the individual ligands. Since the ligands interchange axial and equatorial positions in cis ↔ trans transition, the sign splitting is an immediate consequence of the additivity of the perturbations.

(5) The relative magnitude of the SCF state energy levels is compatible with the conventional ideas on the ligand–metal bonding properties, OH^- being a weaker σ donor but a stronger π donor than CN^-. Indeed, E^a is lower than A_2 (T_{1g} splittings) and E^b is higher than B_2 (T_{2g} splittings); moreover, the T_{2g} splitting is smaller than the T_{1g} splitting. As stressed in the previous section, the state order is not directly evident from the orbital order (Figure 1). Table III shows the two relevant sets of spectral parameters: on the one hand the semiempirical parameters[17,19] and on the other hand "theoretical" parameters, obtained by fitting the Hartree–Fock energy differences to the first-order ligand field expressions. Both tables agree on the sign of $\Delta\sigma$ and $\Delta\pi$, but the SCF calculation assigns the major difference between CN^- and OH^- to the σ interactions, rather than to the π interactions (as does ligand field theory). As a consequence, the specific level orderings based on the two parameter sets of Table III are not completely identical: Table II shows that the sign of the T_{2g} splitting is reversed. The present experimental data do not allow us to prefer one sequence over the other one. It is well to stress that the "Hartree–Fock" LF parameters of Table III are within about 5% of the earlier reported parameters,[4] which were based only on $Co(CN)_6{}^{3-}$ and $Co(CN)_5(OH)^{3-}$. Since the Hartree–Fock value of $\Delta\pi$ is smaller (in absolute value) than the semiempirical $\Delta\pi$ value, our ab initio description corresponds to a smaller π back-bonding for the Co–CN interaction. Still, also at the Hartree–Fock level of approximation, $d\pi$ back-donation remains an important part of the bonding description (as witnessed by the ground-state analysis of Table I, showing a $d\pi$ back-donation of 0.27 electron).

The SCF description of the photochemistry is to a large extent similar to the ligand field description. The photoactive state of the trans complex, $^3E^a$, essentially results from the $(xy,yz) \rightarrow z^2$ excitation; a density difference plot between the photoactive state and the ground state shows the decreased σ donation—and a corresponding bond weakening—of the axial ligands. Since the

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(19) Actually, the semiempirical ligand field parameters of Table III are based on a complete ligand field calculation, including configuration interaction within the d^n states; however, the parameters based solely on the first-order ligand field expressions (which are more relevant in the present context—comparison with Hartree–Fock results) are not significantly different. The average error is on the order of 10%.

Co–OH bonds are known[3,4] to be the weaker bonds even in the ground state, the SCF results agree with the ligand field prediction of axial photolabilization. For the cis complex, the photoactive state, ${}^{3}A_2$, is the result of an $xy \rightarrow x^2 - y^2$ excitation; the corresponding density difference shows the weakening of the equatorial bonds, whereas the axial bonds remain virtually unaffected. Therefore, the calculation suggests a photolabilization of both OH$^-$ and equatorial CN$^-$, without being able to make a quantitative distinction between these two ligands. As far as it goes, the prediction is in qualitative agreement with both experiment and ligand field theory.

V. Concluding Remarks

The qualitative ligand field description of metal–ligand bonding is remarkably well confirmed by the Hartree–Fock calculations. The idea of considering each metal–ligand bond as a more or less independent entity is supported by density difference plots, by orbital energy patterns, and by state energy patterns. It is only slightly affected by the existence of small population differences on the ligand in the different complexes. Quantitatively, the spectral predictions are not satisfactory; it is well-known[20,21] that a better description of the excited states would require a rather extensive treatment of electron correlation. It is gratifying, though, that the general qualitative features of the electronic structure and the energy level pattern are very similar in the Hartree–Fock approximation and in the exact (experimental) description.

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Registry No. $Co(CN)_6^{3-}$, 14897-04-2; $Co(CN)_5(OH)^{3-}$, 16893-73-5; *trans*-$Co(CN)_4(OH)_2^{3-}$, 53769-69-0; *cis*-$Co(CN)_4(OH)_2^{3-}$, 53797-83-4.

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Synthesis, Structure, and Electronic Properties of Tris(propane-1,3-dithiolato) and Tris(ethylene-1,2-dithiolato) Complexes of Niobium(V) and Tantalum(V)

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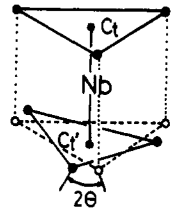
The synthesis and spectroscopic studies of $[A][M(SCH_2CH_2CH_2S)_3]$ and $[A][M(SCH{=}CHS)_3]$ (A = Ph_4P, Et_4N; M = Nb, Ta) and the crystal structure of $[Ph_4P][Nb(SCH_2CH_2CH_2S)_3]$ are presented. Analysis of the IR and Raman spectra of these species as well as of the analogous ethanedithiolate complexes $[A][M(SCH_2CH_2S)_3]$ reveals that the degree of trigonal twist of the MS_6 polyhedron varies in a complicated fashion depending on minute perturbation of crystal-packing forces and electronic factors. Of them the ethylenedithiolate complexes have a geometry closest to the trigonal-prismatic limit. Electronic properties of the dithiolate complexes are examined in terms of CV and electronic spectra and extended Hückel calculations.

Introduction

One of our recent interests has been to explore the chemistry of dithiolate complexes of group 5 transition metals.[1-3] We reported syntheses of the homoleptic ethane-1,2-dithiolate complexes of Nb and Ta, and the X-ray structure analysis of $[Et_4N][Nb(SCH_2CH_2S)_3]$ revealed that the NbS_6 core had a geometry midway between the octahedral and trigonal-prismatic limits.[1b,4] Subsequently these ethane-1,2-dithiolate complexes were found to undergo an unusual rearrangement, via a C–S bond cleavage and a following bond recombination, giving $[MS(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$ (M = Nb, Ta) in good yield in the presence of a trace amount of water, methanol, phenol, etc.[1c,d]

To provide further information concerning the structure and chemical/physical properties of such simple tris(dithiolate) complexes, we have extended our study to those with propane-1,3-dithiolate and ethylene-1,2-dithiolate complexes. This paper reports the detailed synthesis of $[A][M(SCH_2CH_2CH_2S)_3]$ and $[A][M(SCH{=}CHS)_3]$ together with that of $[A][M(SCH_2CH_2S)_3]$ (A = Ph_4P, Et_4N; M = Nb, Ta), their characterization in terms of IR, Raman, CV, and electronic spectra, and the X-ray structure analysis of $[Ph_4P][Nb(SCH_2CH_2CH_2S)_3]$. The IR and Raman spectra are interpreted with the aid of Urey–Bradley type force field analysis, providing us with geometrical information about the MS_6 polyhedron. Further, we discuss the results of CV and electronic spectra using extended Hückel calculations on $[Nb(SCH_2CH_2S)_3]^-$ and $[Nb(SCH{=}CHS)_3]^-$.

Chart I



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