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He I and He II Photoelectron Spectra of Nickel(II), Palladium(II), and Platinum(II) Diethyldithiocarbamate Complexes

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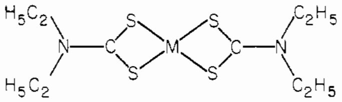
The He I and He II excited photoelectron spectra of M(dtc)$_2$ complexes (M = Zn, Ni, Pd, Pt; dtc = diethyldithiocarbamate) are reported. Assignments of the bands are proposed on the basis of experimental criteria (e.g., He I vs. He II relative intensities) and of qualitative symmetry and overlap considerations. The metal-based or chromophore levels are clearly identified, and an estimate of the complexation perturbations on the chromophore levels is derived. The experimental photoelectron data point to an increase of the π-bonding capability along the series of Ni, Pd, and Pt complexes.

Introduction

Much attention has been focused on Ni(II), Pd(II), and Pt(II) square-planar complexes owing to the large variety of reactions in which they are involved as catalysts.[2] Further interest has been directed to these complexes since the discovery of the anticancer activity of some of them.[3] The knowledge of their electronic structures is a crucial step in order to elucidate their structure-activity relationships. Despite the large number of investigations, however, the electronic properties of this class of molecules are still open to question.[4]

In this paper we report a study of the electronic structures of Ni(II), Pd(II), and Pt(II) diethyldithiocarbamate (dtc) complexes



by means of gas-phase UV photoelectron spectroscopy (UPS). This technique has been widely used in the past few years in studies of complexes with sulfur-containing ligands such as dithiophosphate (dtp),[5,6] difluorodithiophosphate (dfpt),[7] and dithiocarbamate,[8-11] but a sequence of isoelectronic complexes was investigated only in one case.[5] The examination of isoelectronic compounds is convenient because well-known trends in the properties of the metal atoms (such as photoionization cross sections) may help in the interpretation of PE data. Furthermore, the analysis of isoelectronic molecules makes possible comparisons that go beyond a simple one-electron model.[12] In this paper PE data will be discussed on the basis of qualitative symmetry and overlap considerations.

Experimental Section

The methyl ester of dimethyldithiocarbamic acid (hereafter Metc) and the M(dtc)$_2$ (M = Ni, Pd, Pt, Zn) complexes were prepared according to literature methods.[13] Purity was checked by IR and NMR spectroscopy. They were sublimed in vacuo prior to use.

Table I. Ionization Energy Data (eV) and Assignments

	band label	IE	assgnt
Metc	A	8.0	n_s
	A′	8.20	π_3
	B	8.94	π_2
	C	11.08	σ_{SCS}
	D	11.60	π_1
Zn(dtc)$_2$	A	8.13	$n_-(e)$, $\pi_-(a_2 + b_1)$
	B	8.69	$n_+(b_1)$, $\pi_+(e)$
	C	9.30	$n_+(a_1)$
	D	15.8	3d(Zn)
Ni(dtc)$_2$	A	6.79	3d(Ni)
	B	6.97	3d(Ni)
	C	7.76	$\pi_-(b_{3g})$, $\pi_-(a_u)$, $n_-(b_{2u})$
	C′	8.2 (sh)	
	D	8.59	$n_-(b_{1g})$, $n_+(a_g)$, $n_+(b_{3u})$, $\pi_+(b_{2g})$, $\pi_+(b_{1u})$
	D′	9.2 (sh)	
Pd(dtc)$_2$	A	7.18	4d(Pd)
	B	7.54	4d(Pd)
	C	7.86	$\pi_-(b_{3g})$, $\pi_-(a_u)$
	D	8.07	4d(Pd)
	E	8.55	$n_-(b_{2u})$
	F	9.11	$\pi_+(b_{2g})$, $\pi_+(b_{1u})$, $n_+(b_{3u})$
	G	9.55	$n_-(b_{1g})$, $n_+(a_g)$
Pt(dtc)$_2$	A	6.80	5d(Pt)
	B	7.06	5d(Pt)
	C	8.02	5d(Pt), $\pi_-(a_u)$
	D	8.60	$n_-(b_{2u})$
	E	8.86	$\pi_-(b_{3g})$
	F	9.24	$\pi_+(b_{1u})$
	G	9.44	$n_+(b_{3u})$
	H	9.79	$n_+(a_g)$, $\pi_+(b_{2g})$, $n_-(b_{2g})$
	J	10.17	

He I (21.217 eV) and He II (40.814 eV) excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified for He II measurements by inclusion of a hollow cathode discharge lamp, which gives a high photon flux at He II wavelengths (Helectros Development). The spectrometer was connected on line to a MINC 23 computer (Digital Equipment) with an interface built in our laboratory. Data were collected by 3-5 sweeps over 500 distinct channels. Typical sweep times were 5-10 min. The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe, N$_2$, Ar) and to 1s^{-1} He ionization.

Results and Discussion

In order to assign the PE spectra of the studied square-planar complexes, the following strategy was adopted: (i) The knowledge of the valence MOs of the dtc$^-$ anion and of the (dtc)$_2^{2-}$ chromophore was derived by the PE spectrum of Metc (Figure 1) when compared with the spectrum of tetrahedral

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(1) (a) University of Padova. (b) CNR of Padova.
(2) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461.
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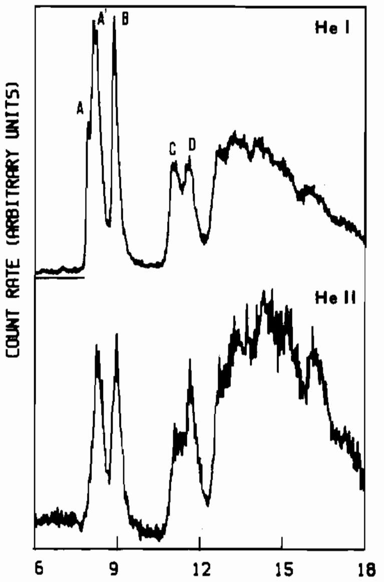

Figure 1. He I and He II excited PE spectra of the methyl ester of dimethyldithiocarbamic acid (Metc).

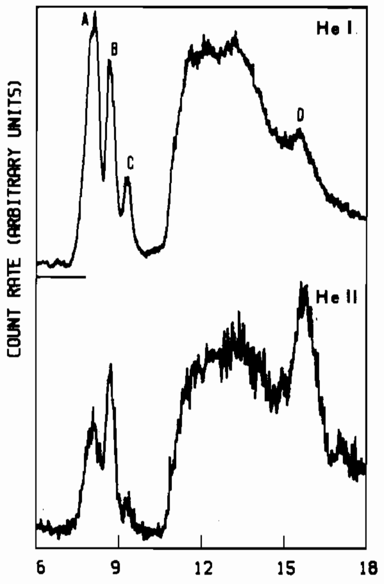

Figure 2. He I and He II excited PE spectra of the Zn(dtc)$_2$ complex.

Zn(dtc)$_2$ (Figure 2). (ii) The interaction between metallic *n*d AOs and the ligand-based combinations were evaluated by qualitative symmetry and group overlap considerations.

Furthermore, He I/He II intensity changes were used in order to assess the participation of ligand and/or metallic *n*d AOs in the corresponding MOs. In this context it is useful to recall the empirical arguments (within the Gelius model[14]) that will be adopted in the following discussion:[15] compared to C and N 2p AOs, sulfur 3s and 3p AOs have drastically lower photoionization cross sections in the He II than in the He I excitation. On the other hand, metallic *n*d AOs strongly increase their relative cross section under He II excitation.

For the sake of clarity we first discuss the chromophore orbitals and then the spectra of the square-planar complexes.

Chromophore Valence Orbitals. The He I and He II excited PE spectra of Metc and of Zn(dtc)$_2$ are shown in Figures 1 and 2, respectively. The pertinent IE values are reported in Table I. Both Metc and Zn(dtc)$_2$ He I spectra have been already reported by other authors.[8,16]

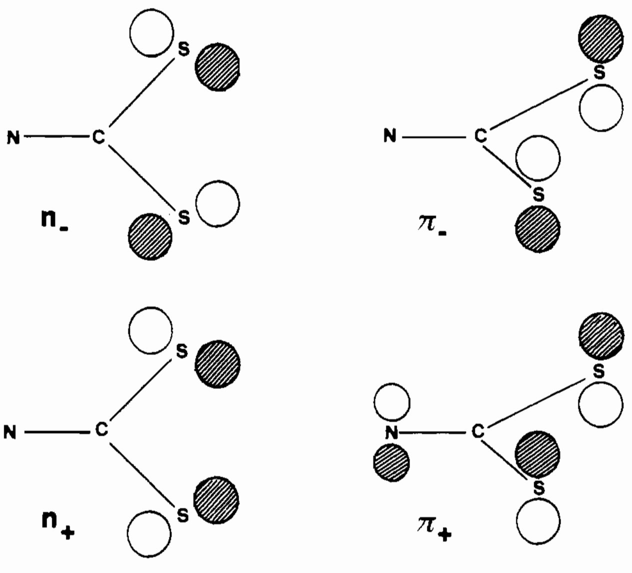

Figure 3. Outer valence MOs of the dtc$^-$ ion.

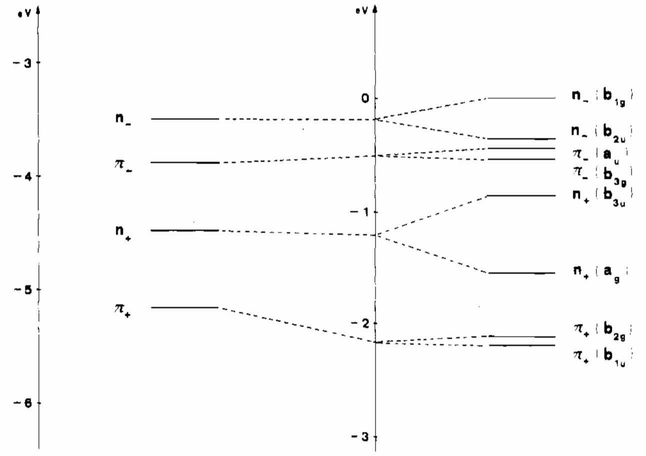

Figure 4. CNDO-computed energy ordering of dtc$^-$ and dtc$_2{}^{2-}$ outer levels.

The five outer valence MOs of Metc, which give rise to the PE bands ranging from 8 to 12 eV, can be described qualitatively as one in-plane sulfur lone pair (n_s), two π MOs mainly localized on the two sulfur atoms (π_2, π_3), one delocalized π_1 MO (to which nitrogen and carbon atoms contribute significantly), and one σ MO strongly localized on the S–C–S moiety (σ_{SCS}). We agree with previous assignments[16] that associate the shoulder A to the n_s ionization and bands A′ and B to π_3 and π_2 ionizations, respectively. On the basis of the He I/He II intensity changes, we also assign band C to the σ_{SCS} ionization and band D to the π_1 one. CNDO type calculations[17] reproduce qualitatively the proposed assignments.

The reported data suggest that the dtc$^-$ MOs, which are energetically accessible for bonding with metal atoms, are those related to n_s, π_3, and π_2 MOs of Metc. These MOs are shown schematically in Figure 3. They represent in-phase and out-of-phase combinations of the in-plane (n_+ and n_-) and out-of-plane (π_+ and π_-) valence orbitals. Their orbital energy ordering from CNDO is $n_- > \pi_- > n_+ > \pi_+$ (Figure 4). The computed orbital energies of the entire (dtc)$_2{}^{2-}$ chromophore (D_{2h}) are also reported in Figure 4 with the MOs shown schematically in Figure 5. As shown in Figure 4, the com-

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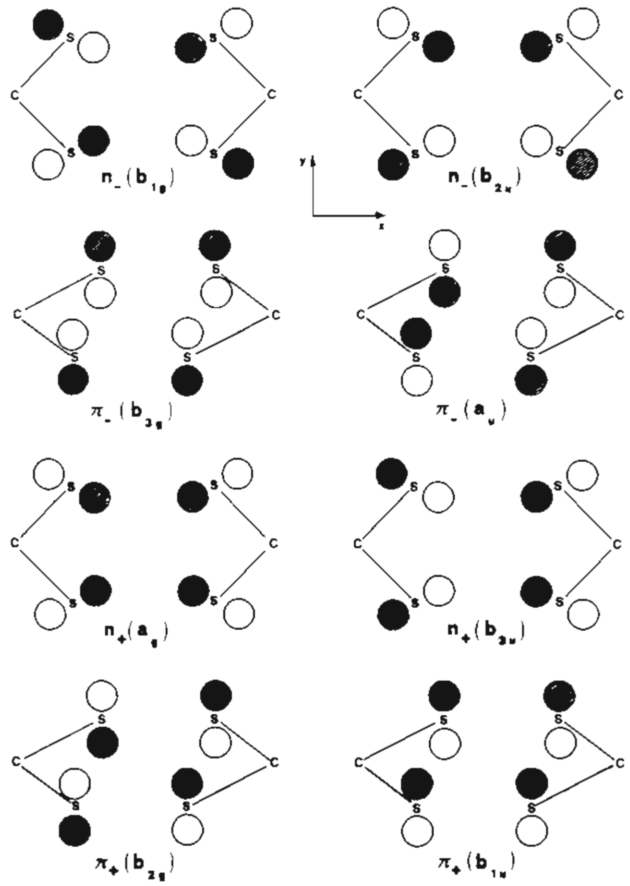

Figure 5. Schematic drawing of the valence basis set of the dtc_2^{2-} chromophore.

puted interligand splitting is negligible for the π_+ and π_- combinations, whereas the largest splitting is for the n_+ combinations.

Obviously, there is no way to check the reported theoretical diagram against experimental data. One approximate method is comparison with PE data of complexes that are "a priori" ionic in character. In such a case the orbital energies related to ligand MOs should, in principle, only shift due to the electrostatic perturbation of the central metal atom and, thus, reproduce the chromophore energy ordering. The pitfall is that no such purely ionic square-planar complex exists. The $Zn(dtc)_2$ complex presents a pseudotetrahedral arrangement (D_{2d}) and can be taken as a test of the dtc^- levels if interligand repulsions are neglected. Since in D_{2d} symmetry the ligand-based valence set spans the irreducible representations $n_+(a_1 + b_2)$, $n_-(e)$, $\pi_+(e)$, and $\pi_-(a_2 + b_1)$, the only significant interligand splitting would be between $n_+(a_1)$ and $n_+(b_2)$.

In the lower IE region of the $Zn(dtc)_2$ PE spectrum (Figure 2), we found three well-resolved bands A, B, and C with an intensity ratio of 4.2:2.4:1. The only way to rationalize this intensity pattern is to assign band A to the $n_-(e)$ and $\pi_-(a_2 + b_1)$ unsplit components, band B to the $n_+(b_2)$ and $\pi_+(e)$ components, and band C to $n_+(a_1)$. This latter component would be stabilized by both interligand interaction and Zn-(4s)–$n_+(a_1)$ mixing, as already suggested for the $Zn(acac)_2$ complex.[18] The He II intensity pattern (5.7:5.9:1) lends support to this assignment since the relative intensity decrease of both A and C bands with respect to B is compatible with a larger sulfur participation in the related MOs. These reported data point to the $n_- \sim \pi_- > \pi_+ \geqslant n_+$ sequence that can be related to the theoretical one for the dtc^- ion (Figure 4) if some stabilization of the n_+ and n_- components by interaction with the 4sp Zn virtual levels is accounted for. The position and the He I/He II behavior unambiguously indicate the 3d Zn character of the prominent band D at 15.8 eV. This further demonstrates the corelike nature of the 3d Zn AOs in $Zn(dtc)_2$.

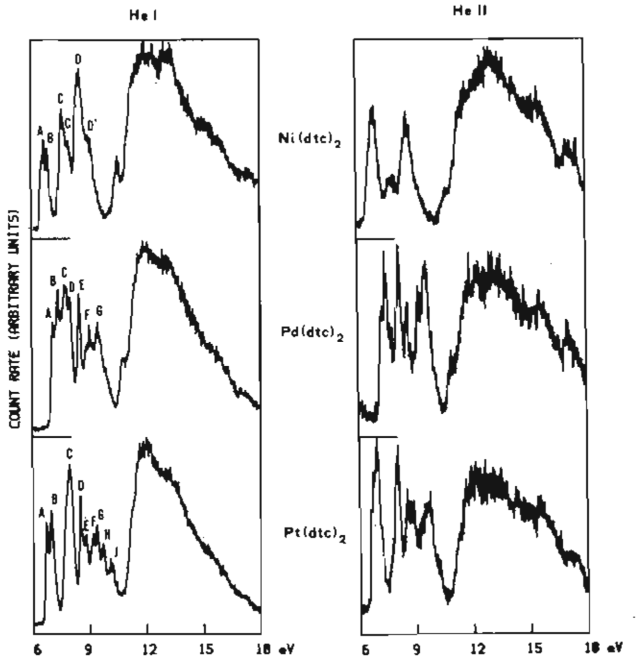

Figure 6. He I and He II excited PE spectra of $Ni(dtc)_2$, $Pd(dtc)_2$, and $Pt(dtc)_2$ complexes.

$M(dtc)_2$ PE Spectra. The He I and He II PE spectra of $M(dtc)_2$ complexes (M = Ni, Pd, Pt) are shown in Figure 6. The pertinent IEs are reported in Table I.

The lower IE region of all the spectra (up to 10.5 eV) is of greatest interest for the metal–ligand interactions. The higher IE region consists of a broad and unresolved band envelope to be associated with inner ligand levels.

In all the spectra of Figure 6, two bands labeled A and B are evident below 8 eV. They are assigned to ionizations from MOs that are mostly composed of d metallic AOs on the basis of the following arguments: (i) In the analogous regions of Metc and $Zn(dtc)_2$, no band was observed, and a destabilization of ligand-based MOs following the complexation would be unreasonable. (ii) The He II intensity of these bands with respect to the higher IE ones increases.

In our opinion, the reported He I/He II data represent the most elegant proof so far achieved for the occurrence of "d" ionizations at lower IEs than for ligand ionizations for this type of coordination compound. In fact, the very low He II cross sections of sulfur AOs allow a more reliable discrimination of metal-based ionizations than in the previously studied oxygen-containing metal chelates.[18]

The same He I/He II comparison allows us to get further information on the *n*d ionizations: whereas in the $Ni(dtc)_2$ case the 3d ionizations are all contained under the nearly degenerate bands A and B, in the case of Pd and Pt analogues we can observe other components at higher IEs, i.e. band D in $Pd(dtc)_2$ and a component of band C in $Pt(dtc)_2$. The experimental pattern of the "d" ionizations is summarized in Figure 7. Some major points are worthy of discussion. The first point regards the spreading of the "d" ionizations, which steadily increases going from Ni to Pd and Pt complexes. Assuming as a gauge of this "d" splitting in Pd and Pt complexes the difference between the mean IE value of bands A and B with that of the inner "d" band, we obtain values of 0.7 and 1.1 eV for Pd and Pt, respectively, whereas the Ni A and B ionizations are only 0.2 eV apart. The values of these

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(18) Fragalà, I.; Costanzo, L. L.; Ciliberto, E.; Condorelli, G.; D'Arrigo, C. *Inorg. Chim. Acta* **1980**, *40*, 15.

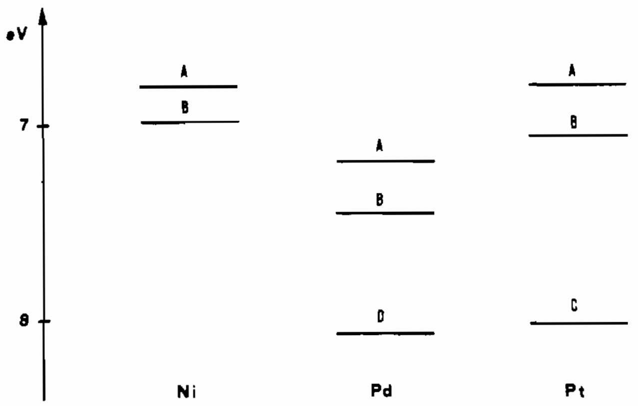

Figure 7. Experimental correlation diagram of the "d" PE bands of $Ni(dtc)_2$, $Pd(dtc)_2$, and $Pt(dtc)_2$ complexes.

Table II. Group Overlap Integrals between the Metallic AOs and the $(dtc)_2^{2-}$ Chromophore

	Ni	Pd	Pt
$\langle n_+ \vert -z^2 \rangle$	0.066	0.174	0.269
$\langle n_+ \vert x^2 - y^2 \rangle$	0.019	0.017	0.046
$\langle n_- \vert xy \rangle$	0.105	0.248	0.470
$\langle \pi_- \vert yz \rangle$	0.032	0.081	0.241
$\langle \pi_+ \vert xz \rangle$	0.048	0.128	0.298

splittings can be compared with those found by Maier et al.[5] for the analogous dtp complexes (Ni = 1.1, Pd = 0.8, Pt = 1.2 eV). Good agreement is found with our results concerning Pd and Pt, whereas a large discrepancy between the data of Ni is evident. This is hardly to be ascribed to a peculiar difference between $Ni(dtc)_2$ and $Ni(dtp)_2$ complexes (see the similarities for the Pd and Pt analogues) and probably is to be imputed to an incorrect assignment of the $Ni(dtp)_2$ spectrum, as already proposed by Andreocci et al.[7] on the basis of the comparison with the spectrum of $Ni(dftp)_2$. Consequently, the agreement between the "d" splitting values obtained by PES and electronic absorption spectroscopy claimed by Maier et al.[5] is erroneous. The very large difference in the "d" splittings of the three different metal atoms is certainly to be related to the expected increase of covalency. Actually, group overlap arguments (see Table II) show that the absolute overlap values increase along the series Ni, Pd, and Pt and, furthermore, that the difference within each "d" set is almost negligible in the Ni complex with respect to those found in the Pd and Pt complexes, in agreement with our PE data. Another point to be discussed refers to the irregular trend in the first IE value along the studied series, which can be explained by two concurrent opposite effects: (a) the large stabilization of d orbitals going from Ni to Pd (Bassett et al.[19] have reported the average of configuration d ionization energies for free Ni, Pd, and Pt (5.88, 8.51, and 8.62 eV, respectively) that indicate very similar values of Pd and Pt with respect to Ni); (b) the increase of covalency going from Ni to Pd to Pt that destabilizes the "d" MOs, since they represent the antibonding counterparts of the metal–chromophore interactions. As a consequence, the highest IE value is pertinent to the Pd case, since the large d energy stabilization overrides the covalent destabilization. It is proper to remember here, however, that the large relaxation contribution, which can be expected for the Ni complex,[20] could be also responsible for the low IE values of the corresponding "d" ionizations.

The reported He I and He II PE data allow us to identify the "d" ionizations, but they do not offer any definitive indication about the nature of the actual d AOs involved in each "d" band of the Pd and Pt spectra. This task would require a reliable quantum-mechanical calculation. In this paper we just give assignments on the basis of the group overlap considerations of Table II. Assuming the axis system of Figure 5, the d_{xy} level is unoccupied and its mixing with the $n_-(b_{1g})$ ligand combination represents the major source of bonding. On the other hand, the $d_{x^2-y^2}$ AO would be almost unperturbed (Table II) and its ionization should be associated with the highest IE "d" band. As far as the remaining "d" AOs (d_{xz}, d_{yz}, and d_{z^2}), the actual assignment is controversial. Two different hypotheses can be put forward: either bands A and B are related to all three d_{xz}, d_{yz}, and d_{z^2} or one of them is to be associated to the inner "d" band. We do not have sufficient arguments to differentiate between these alternatives.[21]

The higher IE bands represent ionizations from the chromophore levels perturbed by interactions by the examined d AOs. This is demonstrated by the intensity decrease with respect to the outer bands. Within this IE region, however, remarkable relative intensity variations are also evident, which suggest a method to identify those chromophore levels (i.e., those having g symmetry) that interact with the metal d AOs.

Starting with the simplest $Ni(dtc)_2$ case, we tentatively assign the bands labeled C and C′ to the $\pi_-(b_{3g})$, $\pi_-(a_u)$, and $n_-(b_{2u})$ levels and the bands D and D′ to the remaining $n_-(b_{1g})$, $n_+(b_{3u})$, $\pi_+(b_{2g})$, and $\pi_+(b_{1u})$ ones. Both the He I relative intensities and the He I/He II changes support this view.

The Pd and Pt spectra present several features that require more detailed discussions. Band C of the $Pd(dtc)_2$ spectrum (which strongly decreases in the He II spectrum) is assigned to the two $\pi_-(b_{3g})$ and $\pi_-(a_u)$ components. The sharp band E, which also decreases in the He II spectrum, is assigned to the nonbonding $n_-(b_{2u})$ orbital. The two remaining F and G envelopes, the second one increasing under He II radiation, are assigned to $\pi_+(b_{2g})$, $\pi_+(b_{1u})$, and $n_+(b_{3u})$ for the former case and to $n_-(b_{1g})$ and $n_+(a_g)$ for the latter case. These assignments have been obtained by assuming the chromophore energy ordering obtained for the $Zn(dtc)_2$ case (i.e., $n_- \sim \pi_- > \pi_+ \geqslant n_+$) and that the Δn_- splitting [$\Delta n_- = \mathrm{IE}(n_-(b_{2g})) - \mathrm{IE}(n_-(b_{2u}))$] is larger than the Δn_+ one (according to the results of Table II). In this hypothesis, approximate experimental Δn_- and Δn_+ values amount to 1 and 0.4 eV, respectively. The $\Delta\pi_+$ and $\Delta\pi_-$ splittings consistently are considered negligible.

The spectrum of $Pt(dtc)_2$ shows several well-resolved components: this fact is certainly a probe of the high covalency of this compound and might give further insights with safe assignments at hand. The lower IE component of band C, which also contains some "d" ionization, is related to the $\pi_-(a_u)$ orbital: note the change of the band shape in the He II spectrum, which supports this assignment. The corresponding $\pi_-(b_{3g})$ interacting level is assigned to the E band since it gains intensity under He II radiation. The larger $\Delta\pi_-$ splitting (0.8 eV) for $Pt(dtc)_2$ than for the Pd complex is in line with the higher π-interacting capability of Pt (see Table II). The sharp band D correlates with band E in the $Pd(dtc)_2$ spectrum and is associated to the nonbonding $n_-(b_{2u})$ component whose interacting $n_-(b_{2g})$ counterpart is to be related to some band of the following complicated nest of bands. In particular, the He II data suggest either band H or J. The F and G components should be assigned to the noninteracting chromophore levels ($\pi_+(b_{1u})$ and $n_+(b_{3u})$), and consistently, the remaining $n_+(a_g)$ and $\pi_+(b_{2g})$ orbitals are associated with bands H and J. Obviously, these latter assignments are tentative and were obtained by assuming the ordering $\Delta n_- >> \Delta\pi_- > \Delta\pi_+, \Delta n_+$, which, in turn, is based on group overlap considerations (Table

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(19) Bassett, P. J.; Higginson, B. R.; Lloyd, D. R.; Lynaugh, N.; Roberts, P. J. *J. Chem. Soc.* **1974**, 2316.

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(21) Accurate intensity ratio measurements between the "d" bands are not possible since the outer chromophore bands strongly overlap with the inner "d" band.

II) once energy-matching corrections between metal d and chromophore levels is accounted for.

Conclusions

The very low photoionization He II cross section of the sulfur-based MOs when compared to the metal-based ones leads us to an efficient identification of the very complicated spectral pattern. In a similar manner, the PE bands associated with the chromophore levels interacting with the d metallic AOs (those of g symmetry) have been identified, so providing an estimate of the complexation perturbations by comparison with the bands of the noninteracting levels (u symmetry). The set of Δn_-, Δn_+, $\Delta\pi_+$, and $\Delta\pi_-$ values obtained in this manner are consistent with the expected chemical behavior of the central metal atom and represent a first rough estimate of the differing σ- and π-bonding capabilities of the Ni, Pd, and Pt atoms.

Acknowledgment. We thank the CNR (Rome) for generous financial support to this research and Prof. E. Tondello for helpful suggestions.

Registry No. Metc, 3735-92-0; $Zn(dtc)_2$, 14324-55-1; $Ni(dtc)_2$, 14267-17-5; $Pd(dtc)_2$, 15170-78-2; $Pt(dtc)_2$, 15730-38-8.

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Infrared Emission Spectra of Alkali Chloroaluminates and Related Melts

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Infrared emission spectra of chloroaluminates and related melts have been recorded with a new technique using thick samples as reference. The molten salt is compressed between a polished nickel piston and a diamond IIa window, and the nickel sample container is sealed with gold O-rings. This system allows infrared emission to be recorded between 50 and 1500 cm^{-1} up to 600 °C and with at least 3 atm of vapor pressure of the sample. The method has been utilized for structural investigations of $AlkAlCl_4$ (Alk = Li, Na, K, Rb, Cs), $KMCl_4$ (M = Al, Ga, In), $AlkAl_2Cl_7$ (Alk = Li, Na, K, Cs), $CsGa_2Cl$, and $NaAlCl_4$–Al_2Cl_6 melts. Increasing perturbation of a tetrahedral $AlCl_4^-$ ion in the series Cs < Rb < K < Na < Li has been inferred from the activation of the totally symmetric stretching vibration, intensity variations in overtones and combination bands, and the position of the anion–cation mode. A scheme for assignment of vibrational transitions called Build Up by Symmetry Correlated Ligands (BUSCL) has been described and applied to the Al–Cl–Al-bridged $Al_2Cl_7^-$ ion. It turns out that probably only Li^+ is able to stabilize a bent bridge and that a linear or limp bridge is preferred with the larger alkali ions.

Introduction

Chloroaluminate melts may be defined as mixtures between aluminum chloride and other metal chlorides. Characteristic of these systems is the formation of complex anions, a feature that is the origin of the well-known acid–base variations and other unique properties. The chloroaluminates are interesting not only from a theoretical point of view but also because they can be utilized in industrial and preparative chemistry where the melts can act as electrolyte, solvent, or catalyst.

The most thoroughly investigated chloroaluminates are the aluminum chloride–alkali chloride melt mixtures. Some of the main features of these molten salts are summarized in Table I. The dominant aluminum species in the basic melts ($X_{AlCl_3} < 0.5$) is $AlCl_4^-$. The acidic mixtures have low melting temperatures and bond properties intermediate between covalent and ionic as demonstrated by the formation of chloroaluminate polymers and an immiscibility gap.[2,3] Potentiometric,[4–6] vapor pressure,[7,8] and Raman spectroscopic[9–11] studies have shown that $AlCl_4^-$, $Al_2Cl_7^-$, $Al_nCl_{3n+1}^-$ ($n \geq 3$), and Al_2Cl_6 are present for $X_{AlCl_3} > 0.5$. From the Raman studies,[9–11] it has been concluded that $AlCl_4^-$ has a tetrahedral structure, while $Al_2Cl_7^-$ and Al_2Cl_6 are composed of two $AlCl_4^-$ tetrahedra sharing one and two corners, respectively. Neither the structure nor the stoichiometry of $Al_nCl_{3n+1}^-$ ($n \geq 3$) has been determined, but usually only $n = 3$ (i.e., $Al_3Cl_{10}^-$) is assumed.

The Raman spectra of aluminum chloride–alkali chloride molten mixtures are well established,[9–11] while little is known about the complementary infrared (IR) spectra necessary for a complete vibrational analysis of the melt structures. Thus, the aim of this work has been to obtain the relevant IR spectra in order to get a better structural characterization of these systems.

Interesting features to be studied are perturbation of the anions by the alkali metal counterions and whether the Al–Cl–Al bridges are linear or bent. The latter is the case in solids containing $Al_2Cl_7^-$ or the corresponding bromide ion, $Al_2Br_7^-$.[12–15] Furthermore, vibrations arising from ionic bonds can only be observed in the IR spectra.[16] Such IR bands have

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