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The Electronic Structures of Bis(*cis*-1,2-dicyano-1,2-ethenedithiolato)nickel Complexes

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The core binding energies of N1s and S2s in *cis*-1,2-dicyano-1,2-ethanedithiolate (maleonitriledithiolate, mnt) complexes were measured by means of X-ray photoelectron spectroscopy (XPS), and the energy differences between N1s and S2s, ΔE, were found to be 171.7—172.6 eV throughout the complexes studied. The lowest ΔE value, 171.7 eV, was shown by $[Ni(mnt)_2]^-$. The electronic structures of $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{2-}$ were calculated by the discrete variational Xα method. The XPS measurements and the molecular orbital (MO) calculations provide consistent results that the oxidation state of the nickel atom is +2 for both nickel mnt complexes and that the highest occupied MO is $5b_{3g}$, which is mainly localized on ligands and which holds an unpaired electron in $[Ni(mnt)_2]^-$.

The metal dithiolate compounds have been of great interest to inorganic chemists because of their remarkable oxidation-reduction behavior, including the formation of abnormal valence states of the metal.[1] A typical dithiolate complex is the *cis*-1,2-dicyano-1,2-ethenedithiolate (maleonitriledithiolate, mnt) complex, in which the metal ion has a wide variety of oxidation states. Usually the oxidation state of the metal in an mnt complex is determined so as to satisfy both the stoichiometry and charge of the complex. For example, the formal oxidation state of Ni in $[Ni(mnt)_2]^-$ may be +3, on the assumption that mnt is a dinegative ion. However, the determination of the oxidation state of the metal in such a way is questionable.

There have been extensive studies of the electronic structure of these compounds by Schupack *et al.*,[2] Schmitt *et al.*,[3] Schlapfer *et al.*,[4] and Kobayashi *et al.*[5] The ESR results suggest that the ground state of $[Ni(mnt)_2]^-$ is $^2B_{3g}$, in which the half-filled out-of-plane π molecular orbital (MO) is extensively delocalized over the ligand.[3] Schlapfer *et al.*[4] measured the force constants of dithiolate complexes and estimated that 38% of the unpaired electron in the highest occupied MO of $[Ni(mnt)_2]^-$ is localized on the metal. The X-ray diffraction results of $[Ni(mnt)_2]^-$ have suggested that the ground state is either ^2A_g or $^2B_{3g}$.[5] An X-ray photoelectron spectroscopic (XPS) study of $[M(S_2C_2R_2)]^{0,1-,2-}$ (M=Ni, Pd, and Pt, and R=CN and C_6H_5) has been reported by Grim *et al.*[6] Judging from the absence of satellites and from the line-width of Ni2p XPS, they pointed out that the reduction did not appreciably change the charge on the metal, giving most of the added electronic charge to the ligands. However, there still remain problems in understanding accurately the electronic structure of mnt complexes. A detailed investigation of the electronic structures of these compounds can be expected to explain the results of ESR, IR, XPS, and so on. It has been shown in a previous work[7] that the energy difference between core orbitals gives information about the charge distribution and the electronic structure of metal complexes. The present paper will describe the results of XPS studies of $[M(mnt)_2]^{2-}$ (M=Co, Ni, Cu, and Zn) and $[M(mnt)_2]^-$ (M=Fe and Ni), and also the results of discrete variational (DV) Xα molecular orbital calculations for $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{2-}$. The energy difference between N1s and S2s and the electronic structures of these nickel complexes are then discussed on the basis of the XPS and DV-Xα results.

Experimental

The complexes, $[M(mnt)_2]^{2-}$ (M=Co, Ni, Cu, and Zn) and $[M(mnt)_2]^-$ (M=Fe and Ni), are all well-known and were prepared by standard methods.[8] The X-ray photoelectron spectra were recorded on a JEOL Model JESCA-3A spectrometer. Magnesium $K\alpha_{1,2}$ radiation (1253.6 eV) was used as the X-ray excitation source, and the measurements were carried out at a vacuum of 5×10^{-7} Torr (1 Torr=133.322 Pa) or below. We obtained the difference between the N1s and S2s binding energies by a synchronous measurement. The measurement was repeated several times for each sample, yielding consistent results. The average of the binding-energy difference was determined, by several runs for a given compound, with an accuracy of about ±0.1 eV.

Computational Method

The computational details of the spin-polarized DV-Xα method have been thoroughly described elsewhere.[9] In the Hartree-Fock-Slater model,[10] the exchange-correlation term is given by:

$$X_{xc\uparrow}(1) = -3\alpha[(3/4\pi)\rho_\uparrow(1)]^{1/3},$$

where $\rho_\uparrow$ (1) is the local charge density with up-spin and where α is the exchange-scaling parameter; the value of $\alpha=0.70$ is used for all atoms throughout the present calculation.[11] The spin-polarized DV-Xα self-consistent-charge (SCC) procedure[9] has been performed for both up and down spins. An approximate self-consistent molecular potential is determined from the Mulliken gross orbital populations. The numerical basis functions for up- and down-spin orbitals are obtained with an atom-like potential constructed by spherically averaging the molecular potential around the nucleus for the region inside each atomic sphere. The basis sets, including Ni1s—4p, C and N1s—2p, and S1s—3d, are utilized for the present calculations.

The molecular geometries of the complexes are de-

Table 1. The electron-binding energies (eV) of N1s and S2s for tetrabuthylammonium salts of $[M(S_2C_4N_2)_2]^{n-}$ (n=2 or 1) and $Na_2S_2C_4N_2$

	Fe^{3+}	Co^{2+}	Ni*	Ni^{2+}	Cu^{2+}	Zn^{2+}	Na^+
N1s	402.5	401.9	400.5	401.2	401.8	401.7	399.9
S2s	230.4	229.7	228.8	228.8	229.2	229.2	226.9
ΔE	172.1	172.2	171.7	172.4	172.6	172.5	173.0
$Ni2p_{3/2}$			857.3	857.3			
$Ni2p_{1/2}$			874.6	874.6			

Ni*: $[Ni(S_2C_4N_2)_2]^-$.

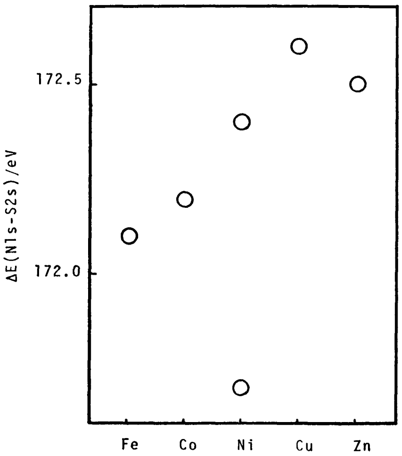

Fig. 1. The correlation between the energy difference, ΔE(N1s−S2s), and the atomic number of the metal in *cis*-1,2-dicyano-1,2-ethenedithiolate complexes.

termined from the experimental results.[5] In the present calculations, the complexes are regarded as having the D_{2h} symmetry.

Results and Discussion

Table 1 shows the N1s and S2s core-binding energies measured for $[M(mnt)_2]^{2-}$ (M=Co, Ni, Cu, and Zn), $[M(mnt)_2]^-$ (M=Fe and Ni), and Na_2mnt. The Ni2p energies are also given for the nickel complexes. Accurate binding energies were not obtained for sulfur $2p_{3/2}$ and $2p_{1/2}$ because of their overlapping. The C1s peaks of the ligand could not be well distinguished from the peaks of various nonequivalent carbon atoms of the tetrabutylammonium ion contained as the counter ion in the sample. The measured values of the binding energies would have to be corrected for the charging and the counter-ion effect, which are hard to evaluate. Thus, the energy differences between them, which are almost free from those effects, are used to give information about the electron distribution in mnt complexes. The energy differences, ΔE, between N1s and S2s is found to be 173.0 eV for the mnt anion and to decrease to 172.6—171.7 eV by coordination to the metal. For a easy comparison of ΔE values between different metal compounds, ΔE is plotted in Fig. 1 against the atomic number of the metal. The observed ΔE value in general increases with an increase in the atomic number (Co(172.2)→Zn(172.5)). An exceptionally low value (171.7) was observed for $[Ni(mnt)_2]^-$, which is of particular interest with regard to its electronic structure. From the core-binding-energy measurements, it is found that: (1) ΔE is decreased by the coordination to the metal, (2) ΔE increases with an increase in the atomic number of the metal, and (3) different ΔE values are obtained for the two nickel complexes.

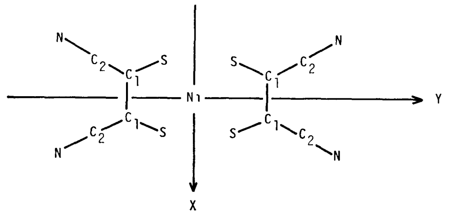

Fig. 2. The structure of mnt and the notations of atoms.

XPS Results and Charge Distributions. First, we will discuss the decrease in ΔE (=E(N1s)−E(S2s)) by the coordination to the metal in a qualitative way. When the ligand coordinates to the metal ion, electron donation takes place from sulfur to metal. The electron population on sulfur then decreases, which deepens the level of the sulfur core orbital in the first approximation, regardless of the other potentials. The ΔE value of Na_2mnt is eventually larger than those of the metal complexes.

Next, we will discuss the ΔE values of the complexes. The relation between the ΔE value and the charge distribution can be discussed in terms of Siegbahn's equation:[12]

$$E_i = E^\circ_i + k_i q_i + \sum_{i \neq j} q_j / r_{ij}. \qquad (1)$$

In this equation, E_i and E°_i are the level energies of the i atom of the complexes studied and that of the reference material; q_i and q_j, the net charge on the i and j atoms respectively, and r_{ij}, the internuclear distance between the i and j atoms. The last term in Eq. 1 represents an interatomic Madelung-type potential. The value of the parameter, k_i depends on the atomic species. Using Eq. 1 and the bond distances previously reported,[5] the binding energies (in eV) for the N1s and S2s can be estimated as follows:

$$E(\mathrm{N1s}) = E^\circ(\mathrm{N1s}) + k_N q_N + 2.60 q_M + 10.78 q_S + 13.21 q_{C1} + 19.76 q_{C2} + 6.28 q_{N}, \qquad (2)$$

$$E(\mathrm{S2s}) = E^\circ(\mathrm{S2s}) + k_S q_S + 6.70 q_M + 12.83 q_S + 19.80 q_{C1} + 13.68 q_{C2} + 10.78 q_{N}, \qquad (3)$$

where the subscripts of q denotes the atomic species as are shown in Fig. 2. Then, we can evaluate the energy differences between N1s and S2s from the following equation:

$$\Delta E(\mathrm{N1s-S2s}) = \Delta E^{\circ}(\mathrm{N1s-S2s}) + (k_{\mathrm{N}}-4.5)q_{\mathrm{N}} - (k_{\mathrm{S}}+2.05)q_{\mathrm{S}} - 4.10q_{\mathrm{M}} - 6.59q_{\mathrm{C1}} + 6.08q_{\mathrm{C2}}. \qquad (4)$$

Here, k_{N} is taken as 21.5 according to Siegbahn *et al.*[12] The value of k_{S} is estimated as 21 on the basis of the 2s—3s one-center integral.[13] Thus, the difference in ΔE between the two complexes can be expressed as follows:

$$\Delta(\Delta E) = 17\delta q_{\mathrm{N}} - 23\delta q_{\mathrm{S}} - 4\delta q_{\mathrm{M}} - 7\delta_{\mathrm{C1}} + 6\delta q_{\mathrm{C2}}, \qquad (5)$$

where δq_{i} is the difference in the effective charge on the i atom between the two complexes. Since the electronegativity of metal increases in going right across the periodic table, the metal net charge gradually decreases, though the value of q_{M} in general remains positive. This negative δq_{M} value causes a positive contribution to $\Delta(\Delta E)$. The less positive metal charge should result in a less negative ligand charge. Since the positive δq_{S} makes a negative contribution to $\Delta(\Delta E)$, opposing the observed trend in ΔE, it is probable that the contribution of δq_{S} is more or less counterbalanced by those of δq_{N}, δq_{C1}, and δq_{C2}.

Finally, the difference in the charge distribution between the two different nickel complexes will be discussed on the basis of the observed ΔE values. The photoelectron spectra show that the nickel $2p_{1/2}$—$2p_{3/2}$ energy separations are almost the same for the two mnt complexes. It has been reported that the splittings of spin-orbit components are often influenced by the oxidation state of the atom, especially for transition-metal ions.[14] If this can be applied to the present case, the almost identical $2p_{1/2}$—$2p_{3/2}$ separations may be taken as reflecting a close resemblance between the nickel electronic states of the two complexes. Thus, the δq_{M} term (with a small coefficient) is assumed to be negligible. Since all the valence electrons existing near the carbon atoms of the mnt^{2-} ligands participate in the bonding, the change in the charge of the complex would have only secondary effects on the charge densities of the carbon atoms. Thus, the δq_{C1} and δq_{C2} terms (with small coefficients) may also be neglected. With these assumptions, Eq. 5 may be approximated by:

$$\Delta(\Delta E) = 17\delta q_{\mathrm{N}} - 23\delta q_{\mathrm{S}}. \qquad (6)$$

In the same way, if the difference in charge between the two nickel complexes is attributed to the difference in the nitrogen and sulphur charges, we obtain:

$$1 = 4\delta q_{\mathrm{N}} + 4\delta q_{\mathrm{S}}. \qquad (7)$$

With the observed $\Delta(\Delta E)$ value of −0.7 eV (=ΔE-($[\mathrm{Ni(mnt)_2}]^{-}$)−ΔE($[\mathrm{Ni(mnt)_2}]^{2-}$)). Eqs. 6 and 7 give:

$$\delta q_{\mathrm{S}} = 0.12 \text{ and } \delta q_{\mathrm{N}} = 0.13.$$

In obtaining these values, it was assumed that the charges on Ni, C_1, and C_2 do not appreciably change when an electron is removed from $[\mathrm{Ni(mnt)_2}]^{2-}$. Although there are good reasons for these assumptions, as has been described above, further examination will be made below by reference to the results of the DV-Xα MO calculations.

TABLE 2. THE CORE-ORBITAL ENERGIES (eV) FOR $[\mathrm{Ni(mnt)_2}]^{2-}$ AND $[\mathrm{Ni(mnt)_2}]^{-}$ FROM DV-Xα CALCULATIONS

	$[\mathrm{Ni(mnt)_2}]^{2-}$	$[\mathrm{Ni(mnt)_2}]^{-}$
Ni2p	−827.8	−833.9
N1s	−371.8	−376.8
S_{2S}	−198.5	−204.3

Results of Molecular Orbital Calculations. Next, the results of DV-Xα MO calculations will be discussed in relation to the above XPS results, with particular reference to the electronic structure of $[\mathrm{Ni(mnt)_2}]^{-}$. Table 2 shows the calculated core orbital energies of the two nickel complexes. In order to obtain accurate ionization energies by the Xα method, calculations should be made of Slater's transition state.[10] The values in Table 2 refer to the ground state and do not allow for the relaxation effects on ionization. Thus, they can not be directly compared with the experimental binding energies. However, they may be expected to give a sufficiently good estimate for the $\Delta(\Delta E)$ value, since the relaxation effects are, for the most part, cancelled out in taking the difference between the two complexes. The values of ΔE are found to be 173.3 and 172.5 eV for $[\mathrm{Ni(mnt)_2}]^{2-}$ and $[\mathrm{Ni(mnt)_2}]^{-}$ respectively; thus, their difference, $\Delta(\Delta E)$, is −0.8 eV, in good agreement with the experimental value of −0.7 eV. The differences in the ΔE values on the DV-Xα calculation are 0.3 eV for Ni2p—S2s and 1.1 eV for Ni2p—N1s, which are comparable with the experimental values of 0.0 and 0.7 eV respectively.

The energies and components of the valence orbitals are given for $[\mathrm{Ni(mnt)_2}]^{2-}$ and $[\mathrm{Ni(mnt)_2}]^{-}$ in Table 3. The positive orbital energies for $[\mathrm{Ni(mnt)_2}]^{2-}$ result from the neglect of the Madelung potentials in the present calculation. The highest occupied molecular orbital (HOMO) for both complexes is the out-of-plane π-type $5b_{3g}$ MO, which consists mainly of S3p atomic orbitals with a minor Ni3d component. It is this orbital from which an electron is removed in going from $[\mathrm{Ni(mnt)_2}]^{2-}$ to $[\mathrm{Ni(mnt)_2}]^{-}$. The occupied MO's, whose main component is a metal d orbital, are $4b_{2g}$ (d_{xz}), $20a_g$ ($d_{x^2-y^2}$), $19a_g$ (d_{z^2}), and $4b_{3g}$ (d_{yz}). Therefore, the nickel atoms in both complexes are considered to have the d^8 configuration or the +2 oxidation state. (In spite of the Ni 3d population being slightly less than 50%, $4b_{2g}{}^{\uparrow}$ should be considered to correspond to Ni d_{xz}, since the rest of the d_{xz} population is mainly found in $3b_{2g}$, which is considered to be a ligand orbital.)

Table 4 lists the Mulliken orbital and overlap populations for $[\mathrm{Ni(mnt)_2}]^{2-}$ and $[\mathrm{Ni(mnt)_2}]^{-}$. The Ni net charges are almost the same for $[\mathrm{Ni(mnt)_2}]^{2-}$ (+0.28) and $[\mathrm{Ni(mnt)_2}]^{-}$ (+0.27). A significant mixing is seen between metal and ligand orbitals, and the net charges are greatly different from the formal charge (+2). The net charges on the sulphur and nitrogen atoms slightly increase on going from the binegative to the uninegative ion. The change in

TABLE 3. THE VALENCE-SHELL MO'S OF $[Ni(mnt)_2]^{2-}$ AND $[Ni(mnt)_2]^-$

Symmetry	Orbital energy	Orbital populations/%											
		Ni			S			C_1		C_2		N	
		3d	4s	4p	3s	3p	3d	2s	2p	2s	2p	2s	2p
$[Ni(mnt)_2]^{2-}$													
$5b_{3g}$	5.02	28.5				58.3	0.7		7.2		1.2		4.0
$4b_{2g}$	3.87	60.5				12.6	3.5		15.1		0.6		7.5
$20a_g$	3.80	85.4	10.0		0.0	3.8	0.3	0.0	0.3	0.0	0.0	0.0	0.0
$6b_{1u}$	3.59			7.5		59.4	2.8		20.5		0.5		9.2
$19a_g$	3.40	84.9	0.1		2.2	1.8	5.0	0.8	0.4	0.0	0.1	0.0	0.3
$4b_{3g}$	3.05	65.0				14.7	1.5		12.9		0.0		5.9
$16b_{3u}$	3.02			4.5	1.4	90.1	0.7	1.3	0.9	0.0	0.0	0.0	1.0
$3a_u$	2.78					69.3	1.3		19.5		0.0		9.8
$17b_{2u}$	2.50			8.6	0.3	84.3	1.5	0.7	0.2	1.5	1.4	0.0	1.4
$3b_{2g}$	1.96	28.9				58.6	0.5		7.4		0.1		4.5
$14b_{1g}$	1.74	36.6			5.2	54.0	0.4	1.5	2.0	0.0	0.0	0.0	0.2
$18a_g$	1.03	10.9	10.1		5.2	65.8	1.7	0.0	2.6	0.9	1.3	0.3	0.9
$3b_{3g}$	0.83	3.9				20.7	1.2		31.4		8.3		34.3
$5b_{1u}$	0.80			1.7		24.0	0.5		30.0		8.7		34.5
$13b_{1g}$	0.25	12.4			5.1	32.9	2.8	3.3	18.7	1.5	6.0	2.8	14.3
$16b_{2u}$	0.09			0.2	10.9	28.3	2.3	0.9	27.2	0.0	6.2	0.0	24.0
$[Ni(mnt)_2]^-$													
$5b_{3g}\uparrow$	−0.47	17.9				64.3	0.2		11.6		0.7		5.3
$4b_{2g}\downarrow$	−1.61	52.0				23.8	2.6		14.7		0.0		6.8
$6b_{1u}\downarrow$	−1.67			7.7		53.9	3.1		24.4		0.0		10.7
$6b_{1u}\uparrow$	−1.77			7.4		52.4	3.2		25.6		0.0		11.3
$4b_{2g}\uparrow$	−1.82	48.9				28.2	2.2		14.1		0.0		6.6
$20a_g\downarrow$	−1.87	82.5	10.7		0.3	5.8	1.1	0.0	0.4	0.0	0.0	0.0	0.0
$20a_g\uparrow$	−2.14	81.2	10.8		0.3	6.9	0.0	0.0	0.5	0.0	0.0	0.0	0.0
$16b_{3u}\downarrow$	−2.34			4.5	2.1	89.8	0.4	1.3	0.9	0.0	0.0	0.0	0.9
$19a_g\downarrow$	−2.34	80.8	0.1		2.9	3.3	4.2	0.7	4.6	0.0	0.0	0.0	1.4
$3a_u\downarrow$	−2.48					71.8	1.1		17.5		0.1		9.4
$16b_{3u}\uparrow$	−2.49			4.6	2.1	89.7	0.4	1.3	0.9	0.0	0.0	0.0	0.9
$4b_{3g}\downarrow$	−2.55	68.4				6.1	1.6		15.8		0.1		8.0
$3a_u\uparrow$	−2.60					72.8	1.1		16.6		0.2		9.2
$19a_g\uparrow$	−2.62	82.7	0.0		2.9	3.5	3.9	0.7	4.7	0.0	0.0	0.0	1.4
$4b_{3g}\uparrow$	−2.77	68.8				3.7	1.6		16.7		0.3		9.0
$17b_{2u}\downarrow$	−2.99			8.6	0.9	82.8	1.8	0.6	0.4	1.4	1.6	0.2	1.6
$17b_{2u}\uparrow$	--3.13			8.6	0.9	82.6	1.7	0.6	0.5	1.4	1.7	0.2	1.7
$3b_{2g}\downarrow$	−3.56	40.4				49.5	1.0		4.4		0.7		4.0
$3b_{2g}\uparrow$	−3.76	44.4				46.2	1.1		3.6		0.8		3.9
$14b_{1g}\downarrow$	−3.78	32.3			8.4	52.2	0.6	2.0	3.6	0.0	0.2	0.0	0.4
$14b_{1g}\uparrow$	−3.97	31.3			8.8	51.7	0.7	2.1	4.3	0.1	0.3	0.2	0.5
$5b_{1u}\downarrow$	−4.29			2.2		26.3	0.6		21.7		13.6		35.6
$3b_{3g}\downarrow$	−4.29	8.2				22.7	1.3		20.7		13.0		34.0
$5b_{1u}\uparrow$	−4.34			2.3		27.4	0.6		20.0		14.1		35.5
$3b_{3g}\uparrow$	−4.36	10.5				23.6	1.3		18.1		13.4		33.1

sulphur charge is about 0.13, in accordance with the value (0.12) obtained from the XPS results by means of Siegbahn's equation. The change in the N net charge is about 0.10 (0.13), while those in the C_1 and C_2 charges are 0.03 (0.0) and −0.02 (0.0) respectively (the numerals in parentheses being the values obtained or assumed in the preceeding section). By substituting these calculated δq values into Eq. 5, we obtain the $\Delta(\Delta E)$ value of −0.9 eV, in good agreement with the XPS result of −0.7 eV and with the value of −0.8 eV obtained directly from the calculated orbital energies. The good agreements between the calculated and the XPS values demonstrated above add support to our estimate of the charge-density distribution and to our arguments made in the interpretation of the XPS results, including the idea that the electronic state of the nickel ion in $[Ni(mnt)_2]^-$ is very similar to that in $[Ni(mnt)_2]^{2-}$. The spin density on the S atom is calculated to be 0.14, which supports the conclusion from the ESR results

TABLE 4. THE MULLIKEN POPULATIONS FOR $[Ni(mnt)_2]^{2-}$

		$[Ni(mnt)_2]^{2-}$	$[Ni(mnt)_2]^-$		
			Total	Up-spin	Down-spin
Ni	3d	8.549	8.528	4.382	4.146
	4s	0.597	0.593	0.295	0.298
	4p	0.578	0.608	0.304	0.304
Atomic charge		+0.276	+0.271		
S	3s	1.825	1.827	0.914	0.913
	3p	4.166	4.025	2.095	1.930
	3d	0.158	0.165	0.082	0.083
Atomic charge		−0.149	−0.017		
C_1	2s	1.056	1.056	0.528	0.529
	2p	3.138	3.112	1.565	1.547
Atomic charge		−0.194	−0.168		
C_2	2s	0.904	0.890	0.445	0.445
	2p	2.794	2.815	1.407	1.407
Atomic charge		+0.302	+0.295		
N	2s	1.714	1.716	0.858	0.858
	2p	3.814	3.713	1.861	1.852
Atomic charge		−0.528	−0.429		
Bond-overlap populations					
Ni-S		0.515	0.530		
S-C_1		0.625	0.659		
C_1-C_2		0.889	0.858		
C_2-N		1.561	1.586		

TABLE 5. THE BOND LENGTHS (Å) AND FORCE CONSTANTS (mdyn/Å) FOR $[Ni(mnt)_2]^{2-}$ AND $[Ni(mnt)_2]^-$ (1 mdyn$=1\times10^{-8}$ N)

	Bond lengths[5]		Force constants[4]	
	$[Ni(mnt)_2]^{2-}$	$[Ni(mnt)_2]^-$	$[Ni(mnt)_2]^{2-}$	$[Ni(mnt)_2]^-$
Ni-S	2.176	2.147	1.27	1.53
S-C_1	1.732	1.727	2.98	3.20
C_1-C_1'	1.360	1.367	5.49	4.99
C_1-C_2	1.428	1.420	3.86	3.48
C_2-N	1.147	1.133		

obtained by Schmitt *et al.*[3] that the $3p_z$ spin population of the S atom is high.

The $5b_{3g}$ MO is shown schematically in Fig. 3 using the results of MO calculation for $[Ni(mnt)_2]^-$. In this MO, the interactions between Ni–S, S–C_1, and C_2–N are antibonding, while those in C_1–C_2 and C_1–C_1' are bonding. This suggests that the removal of one electron from $5b_{3g}$ MO strengthens the Ni–S, S–C_1, and C_2–N bonds, but weakens the C_1–C_2 and C_1–C_1' bond. The changes in the bond overlap populations given in Table 4 are consistent with this MO argument, demonstrating that the bond-overlap population is useful for a qualitative discussion of chemical bonding. The force constants and the bond lengths of the two nickel mnt complexes measured by Schlaper *et al.*[4] and Kobayashi *et al.*[5] are given in Table 5. The force constants increase, and the bond lengths decrease, as the bond becomes stronger. Their experimental results are consistent with the calculated bond-overlap populations except for the C_1–C_2 bond. (For this bond, however, their experimental results contradict each other; that is, the force constant increases in spite of the increase in bond length in going from $[Ni(mnt)_2]^{2-}$ to $[Ni(mnt)_2]^-$.)

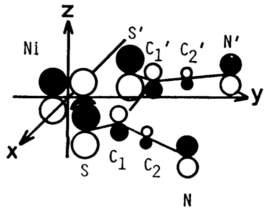

Fig. 3. The $5b_{3g}$ MO with an unpaired electron in $[Ni(S_2C_4N_2)_2]^-$. The black and white circles show positive and negative signs, respectively.

Conclusion

The XPS measurements have been performed in order to obtain the core binding energies for the N1s and S2s of metal mnt complexes. The DV-Xα MO calculations for two Ni complexes have also been carried out in an attempt to explain the chemical shift and the electronic structure of $[Ni(mnt)_2]^-$. The XPS measurements and the MO calculations provide consistent results that the oxidation state of the nickel atom is +2 for both $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{2-}$. The HOMO is $5b_{3g}$, which is mainly localized on ligands and which holds an unpaired electron in $[Ni(mnt)_2]^-$. This is consistent with other spectroscopic results, such as IR and ESR, and also with the X-ray diffraction data.

The computations reported in this paper have been carried out on the HITAC M-180 computer of the Institute for Molecular Science. This work was supported in part by a Grant-in-Aid for Scientific Research No. 510806 from the Ministry of Education, Science and Culture.

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$$\Delta(\Delta E) = 17\delta q_N - 16\delta q_S - 4\delta q_M - 7\delta q_{C1} - 6\delta q_{C2} \qquad (5')$$

and:

$$\Delta(\Delta E) = 17\delta q_N - 16\delta q_S,$$

in place of Eqs. 5 and 6. With Eq. 7, we obtain $\delta q_S = 0.15$ and $\delta q_N = 0.10$.

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