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Study of One-Dimensional Metal Complexes: $K[Ni(mnt)_2]\cdot H_2O$ and $K[Pt(mnt)_2]\cdot H_2O$

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The crystal structure, electrical conductivity and electronic and IR absorption spectra of two metal complexes, $K[Ni(mnt)_2]\cdot H_2O$ and $K[Pt(mnt)_2]\cdot H_2O$ (mnt=1,2-dicyano-1,2-ethylenedithiolato, $C_4N_2S_2{}^{2-}$) were investigated. These two metal complexes belong to orthorhombic system and the lattice constants are a=12.00 Å, b=28.85 Å, and c=3.90 Å for the Ni complex and a=12.11 Å, b=29.23 Å, and c=7.73 Å for the Pt complex. Despite the same stoichiometries and similar crystal structures, the conductivity of Pt complex is 10^3 times as high as that of the Ni complex. The difference in the conductivity between the Ni and Pt complexes may be explained from the density of the unpaired electron on the central metal. The effects of the central metal on the electrical conduction properties may not be negligible for this type of complexes.

In the last decade, many quasi-one-dimensinal (1-D) compounds have been synthesized and intensively studied[1] in order to look for new materials having novel properties. Furthermore, these 1-D systems have stimulated theoretical investigations.

Among these 1-D compounds, typical examples are the 1-D platinum complexes, such as $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP(Br)) and the selenium donor organic metals, such as $(TMTSF)_2ClO_4$ (TMTSF=tetramethyltetraselenafulvalene). In these complexes, the constituent planar molecules form columnar stack structures, which lead to highly directional intermolecular d_{z^2} or π orbital interaction and, consequently, 1-D electronic nature.

As mentioned above, the planarity of molecule is necessary to form a stack with large intermolecular interactions. For this reason, the metal dithiolate complex can be used as a constituent planar molecule and expected to form a 1-D electrical conductor. In addition, these metal dithiolate complexes have unusual redox properties,[2–5] whereas we have taken notice of following two characteristic features:

i) This system has the capacity for structural modifications through changes in the central metal, the ligand substituent, and the counter cation; these chemical modifications are expected to produce a rich variety of new compounds with interesting electrical properties.

ii) The planar molecules have both metal d_{z^2} and ligand p_z orbitals; from this reason, Little suggested that this system is one possible example of the model of excitonic superconductors.[6] Although the real system is not necessarily satisfied with his criterion, this possibility cannot be perfectly excluded.

In fact, Underhill and Ahmad[7] have succeeded in synthesizing a new type of 1-D metallic complex with the mnt ligand; $Li_{0.8}(H_3O)_{0.3}[Pt(mnt)_2]\cdot 1.7H_2O$ (mnt=1,2-dicyano-1,2-ethylenedithiolato, $C_4N_2S_2{}^{2-}$). The crystal structure and physical properties[8–13] of this salt have indicated that it is similar to the sulfur donor organic metals rather than to the 1-D platinum complexes. This conduction pathway is attributed to the overlap of delocalized MO's within the whole anions in which S p_z orbitals in the ligands play a dominant role and the central metal Pt plays a minor role in its conduction. The contribution of the central metal to its physical properties are still uncertain and the partial oxidation state of this system is not fully described.

We intended to elucidate the role of the central metal in the electrical conduction of these metal dithiolate complexes. For this purpose, we chose the cyano-substituted complex (Fig. 1) from a following reason: In the metal dithiolate complexes the electron density is always larger on the ligand than on the metal, but in this cyano-substituted Ni complex the density on the metal is not so small compaired with that on the ligand; these results were suggested by Schläpfer and Nakamoto.[14] We synthesized two metal complexes, $K[Ni(mnt)_2]\cdot H_2O$ and $K[Pt(mnt)_2]\cdot H_2O$, which will be abbreviated as KNi(mnt) and KPt(mnt), respectively. Because the metal d orbitals of KPt(mnt) are more extended than those of KNi(mnt), it is expected that the differences of two central metal are reflected in those of electrical properties.

In this paper, we report the syntheses, crystal structures, electrical conductivity behaviors, optical absorption spectra, and IR spectra of KNi(mnt) and KPt(mnt). From these data, we have considered the central metal effects on the electrical conduction properties for this type of complexes.

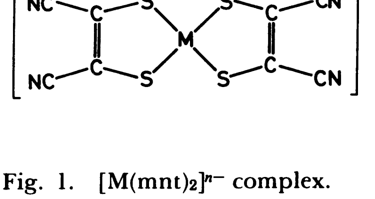

Fig. 1. $[M(mnt)_2]^{n-}$ complex.

Experimental

Preparation. The mnt^{2-} ligand was prepared following a procedure which is the combination of those described by Bray et al.[15] and Davison and Holm.[16] $[Et_4N]_2[Ni(mnt)_2]$ was prepared following a procedure described by Billig et al.[17] KNi(mnt) was prepared by use of a similar procedure of Ahmad and Underhill[8] described below. Slow O_2 oxidation of a solution of $K_2[Ni(mnt)_2]$ (ca. 10^{-3} mol dm^{-3}) in acetone–water (1 : 1) or (2 : 1) gave a black microcrystalline product. Oxidation by oxidant of H_2O_2 or slow evaporation on a steam bath gave the same results. KPt(mnt) may be prepared in a similar method described above, but we used a direct mixing at 50—70 °C of K_2PtCl_4 in aqueous solution and $Na_2(mnt)$ in EtOH-water (1 : 1). Obtained green-black precipitate was filtered off and washed with cold water.

The needle-like crystals of both KNi(mnt) and KPt(mnt) are dichroic with dark brown and green for polarized light parallel and perpendicular to the needle axis, respectively, under microscope. Both samples were stored in a moist (81% relative humidity) atmosphere to prevent dehydration.

Calcd for $KNiS_4C_8N_4H_2O$: C, 24.25; H, 0.51; N, 14.14; K, 9.9; Ni, 14.81; H_2O, 4.55%. Found: C, 24.32; H, 0.55; N, 14.05; K, 9.9; Ni, 13.8; H_2O, 4.35%. Calcd for $KPtS_4C_8N_4H_2O$: C, 18.04; H, 0.38; N, 10.52; K, 7.34; Pt, 36.63; H_2O, 3.49%. Found: C, 17.99; H, 0.38; N, 10.22; K, 7.0; Na, 0.08; Pt, 33; H_2O, 3.44%. Carbon, hydrogen, and nitrogen analyses were carried out by the Laboratory for Organic Elemental Microanalysis of Kyoto University.

Structure. The space group and lattice constants of KNi(mnt) were determined from X-ray oscillation photographs around the needle axis and X-ray Weissenberg photographs. The lattice constants were more accurately determined from X-ray powder diffraction patterns. The lattice constants of KPt(mnt) were determined from X-ray powder diffraction patterns by using those of KNi(mnt) as a guide.

Electrical Conductivity. The d.c. electrical conductivity measurements were performed on polycrystalline samples with two-probe method. Samples were prepared by pressing powders under pressure of $(2.0—2.9)\times10^8$ GPa into cylindrical pellets, 10 mm in diameter and typically 0.5 mm in thickness. Electrical contacts to the disc planes by wetting gold wires with gold-paste (Tokuriki Chemical Research, No. 8560-1A). In order to prevent dehydration, samples were thinly covered with Apiezon N grease. For KPt(mnt), measurements parallel to the disc planes were also performed by cutting a pellet into a rectangular slice in order to evaluate the anisotropy in the conductivity. It is possible in such a case that microcrystalline needles are not oriented randomly but arranged nearly parallel to the disc planes in the compressed pellets. All samples gave ohmic behavior under the conditions of measurement.

IR and Electronic Spectra. The IR spectra were recorded on a Jasco Model IRA-1 (650—4000 cm^{-1}) in KBr pellets. Frequency reading was calibrated by recording the spectra of polystyrene film and the accuracy was about ±1 cm^{-1}.

The solid-state electronic spectra were recorded on a Cary 17D grating spectrometer (4000—33000 cm^{-1}) in KBr pellets.

DSC Measurement. The DSC measurements were performed with a Rigaku DSC-10A apparatus between 110K and 450K, scanning rate 3 or 5 °C min^{-1}.

Results and Discussion

Crystal Structure. Structural Analysis of KNi(mnt). Single crystals (typical size: $0.5\times0.14\times0.01$ mm) coated with a thin layer of paraffin were used for the measurements. A careful inspection of the intensities of oscillation and Weissenberg photographs showed the Laue group *mmm*. The systematic absences $hk0$, $h=2n+1$ and $0kl$, $k+l=2n+1$ indicated two possible space groups: $Pn2_1a$ or *Pnma*. Unfortunately, because of the smallness in size of the crystals it has not been possible to obtain information on the space group for KPt(mnt).

Crystal Structure. The lattice constants of KNi(mnt) and KPt(mnt) are shown in Table 1 together with the values of $[NH_4][Ni(mnt)_2]\cdot H_2O$ reported by Isett et al.[18] They belong to orthorhombic system and have similar crystal structures. For KNi(mnt), there were no diffuse lines in oscillation photographs, which indicates that uniform spacing of the $[Ni(mnt)_2]^-$ anions along the c-axis. However, the $[Ni(mnt)_2]^-$ planes are probably tilted with respect to the c-axis as is often seen for other dithiolate complexes so that the plane-to-plane separation is decreased from 3.90 Å. On the other hand, the X-ray powder diffraction pattern and broadening of the C=C stretching modes on KPt(mnt) (see the section of IR Spectra) suggest a dimerization of the unit cell in the chain direction, the c-axis, which is similar to the fact that $Rb[Pt(mnt)_2]\cdot 2H_2O$[19] posesses a dimerized stack structure. In order to clarify this, the single crystal measurements are necessary and now in progress. Anyway, KPt(mnt) and KNi(mnt) have similar crystal structures, except the possibility of dimerization.

From Table 1, it is clear that there are significant similarities in the crystal structure between KNi(mnt) and $[NH_4][Ni(mnt)_2]\cdot H_2O$, which seems reasonable considering the comparable size of the cations (K^+, 1.33 Å; NH_4^+, 1.48 Å[20]). However, the conductivity for compressed pellets of NH_4 salt (5×10^{-3} S cm^{-1}) is 10^4 times as high as that of K salt (ca. 10^{-7} S cm^{-1}, vide infra). Although the space group of NH_4 salt is unknown, it is probable that the ability of NH_4^+ ions to form hydrogen-bonding networks causes some

Table 1. Crystal Data of KNi(mnt), KPt(mnt) and $[NH_4][Ni(mnt)_2]\cdot H_2O$

	KNi(mnt)	KPt(mnt)	α-NH_4-Ni(mnt)[18]
Chemical Formula	$K[Ni(mnt)_2]\cdot H_2O$	$K[Pt(mnt)_2]\cdot H_2O$	$[NH_4][Ni(mnt)_2]\cdot H_2O$
a/Å	12.00	12.11	12.10
b/Å	28.85	29.23	29.26
c/Å	3.90	7.73	3.92
Space Group	$Pn2_1a$ or *Pnma*	—	—
Z	4	8	4

subtle change in arrangement of the $[Ni(mnt)_2]^-$ monoanions, which causes large difference in the conductivity between NH_4 salt and K salt.

Electrical Conductivity. The experimental results of the electrical conductivity σ are shown in Fig. 2. In both complexes, thermally activated semiconducting behaviors were observed at all temperature. At room temperature, the value of KNi(mnt) is ca. 10^{-7} S cm^{-1}, whereas that of KPt(mnt) is 10^{-4} S cm^{-1}. The activation energy E_a was obtained by a least-squares fit to the usual equation, $\sigma=\sigma_0\exp(-E_a/k_BT)$, with E_a=0.33—0.37 eV (between 300—230 K) for KNi(mnt), whereas E_a=0.18 eV (between 300—200 K) for KPt(mnt). The value of KNi(mnt) is in agreement with that obtained by Underhill et al. ($\sigma_{r.t.}$=*ca.* 10^{-6} S cm^{-1}. E_a=0.346 eV)[21] on single crystals. In addition, observed anisotropy in the conductivity for KPt(mnt) was 10—20, which is considered as a lower limit (see Experimental section).

First, we will discuss the dependence of the conductivity on the central metal. Despite the same stoichiometries and similar crystal structures, the conductivity of KPt(mnt) differs significantly from that of KNi(mnt). However, caution must be paid in interpretation of these results because our measurements were made on compressed pellets; Rosseinsky and Malpas[22] have found that in some intervalence mixtures of more conductive $[Ni(mnt)_2]^-$ monoanion and less conductive $[Ni(mnt)_2]^{2-}$ dianion salts, the conductivities are enhanced; in the mixture with the best conduction, 10^3 times higher conductivity relative to the $[Ni(mnt)_2]^-$ monoanion salt was observed. In order to confirm this, we studied the IR spectra of KPt(mnt), which showed no evidence of the presence of $[Pt(mnt)_2]^{2-}$ dianions (see Fig. 4). Therefore, the sample of KPt(mnt) obtained was not such a mixture but was a genuine compound having the formula of $K[Pt(mnt)_2]\cdot H_2O$. Furthermore, very recently, similar results have been obtained for other metal complexes with the sulfur containing ligands, such as $Li_x[M(mnt)_2]\cdot nH_2O$ (M=Ni, Pd, Pt; for M=Pt, $Li_{0.8}(H_3O)_{0.3}[Pt(mnt)_2]\cdot 1.7H_2O$)[23] and TTF$[M(dmit)_2]_n$ (for M=Ni and Pd, n=2; for M=Pt, n=3; TTF=tetrathiafulvalene; H_2dmit=4,5-dimercapto-1,3-dithiol-2-thione),[24] which indicate that their central metals have considerable effects on conductivity. Our results show that it is inappropriate to ignore the role of the central metals of the metal mnt complexes with integral oxidation states as well as those with non-integral oxidation states.

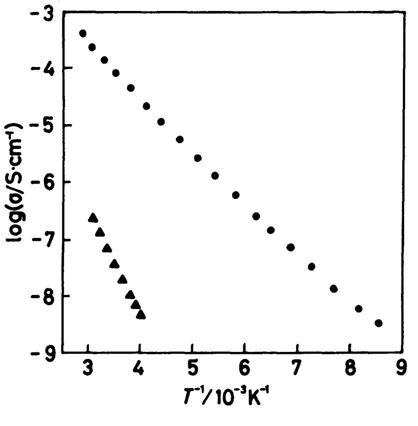

Fig. 2. Electrical conductivity of KNi(mnt) (▲) and KPt(mnt) (●).

Next, we will mention that effects of the ligand substituent R are important in the metal dithiolate complexes of the form $[M(S_2C_2R_2)_2]^-$. Table 2 shows the conductivity of alkali metal salts containing monoanions. Although for R=H and Ph (Ph=C_6H_5) the crystal structures are unknown and an exact comparison cannot be made, it is possible to point out that only the cyano-substituted complexes, namely the metal mnt complexes, show significant dependence of the conductivity on the central metals. This can be explained in terms of the difference of the electron distribution within the whole anion. From the IR spectra of $[Ni(S_2C_2R_2)_2]^z$ series (R=H, Ph, CF_3, and CN; z=0, 1− and 2−) and their normal coordinate analyses, Schläpfer and Nakamoto[14] have argued that in monoanion salts the density of the unpaired electron on the Ni atom increases in the order of R=H<Ph<CF_3<CN. Therefore, it can be interpreted that in R=CN the role of the central metal in the conductivity is significantly large compared with those in other complexes and the difference between Ni and Pt atom is directly reflected in the conductivity; on the other hand, in R=H and Ph the central metals have minor roles in determining the conductivity.

At this point, one question that arises is why the conductivity of the Pt complex, KPt(mnt), is higher than that of the Ni complex. We will discuss this problem in the section of General Discussion.

Electronic Spectra. The solid-state and solution electronic spectra of KNi(mnt) and KPt(mnt) are shown in Fig. 3. Our result of the solution spectra of KNi(mnt) is in agreement with that of $[n\text{-}Bu_4N][Ni(mnt)_2]$ by Shupack et al.[27] For both Ni and Pt complexes, the spectra of a very dilute solution were

Table 2. Conductivity of $[M(S_2C_2R_2)_2]^-$ Monoanions with Alkali Metal Cations

Compound	$\sigma_{r.t.}$/S cm^{-1} a)	
	M=Ni	M=Pt
$Cs[M(S_2C_2H_2)_2]$	1.4×10^{-7} 25)	8.3×10^{-7} 25)
$K[M(S_2C_2Ph_2)_2]$	1×10^{-7} 26)	$\sim10^{-6}$ 26)
$K[M(S_2C_2(CN)_2)_2]\cdot H_2O$	$\sim10^{-7}$	1×10^{-4}

a) All measurements were made on compressed pellets.

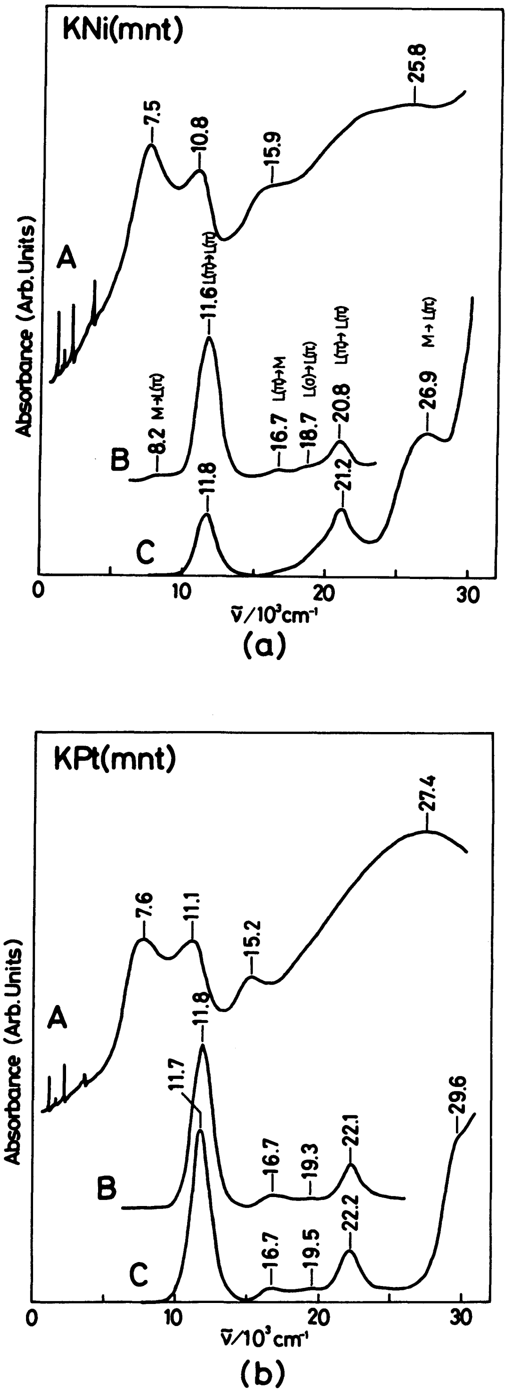

Fig. 3. Electronic spectra of (a) KNi(mnt) and (b) KPt(mnt): A, Solid-state spectra in KBr pellets; B, in acetonitrile solution; C, in acetone–water (1:1) solution. In the acetone–water (1:1) solution, very intense absorptions due to solvent made it impossible to measure below ca. 8000 cm^{-1}. In the case of the Ni complex, the assignments of solution spectra by Schrauzer and Mayweg[28] are also shown: L(π)=ligand π orbital dominant MO, L(σ)=ligand σ orbital dominant MO, M=metal d orbital dominant MO.

almost the same with Fig. 3, suggesting the presence of monomeric [M(mnt)$_2$]$^-$ species in solution. Moreover, the band positions are essentially the same in both acetone–water (1:1) and acetonitrile solutions. In the solution spectra of [Ni(mnt)$_2$]$^-$ monoanion, the assignments by Schrauzer and Mayweg[28] are also shown in Fig. 3 (a).

First, we will look at the results of the solid-state spectra of KNi(mnt) and KPt(mnt). In contrast with the significant differences in the conductivity, the solid-state spectra of both complexes are very similar. This is partly due to the intense absorptions involving the ligand-dominant orbitals, such as L(π)→L(π) transition. The differences of both Ni and Pt complexes which appear in solution spectra are smeared in the solid-state spectra. From the solid-state spectra, we could not find any marked differences in contrast to the conductivity.

Next, we compare the solid-state spectra of both complexes with their solution spectra. As the solid-state electronic bands are appreciably diffused and continuously overlap with each other, it is difficult to find the correspondence between the bands of the solid-state spectra and of solution spectra. However, in the solution spectra of both complexes there is no band observed corresponding to the lowest-energy bands around 7500 cm^{-1} in solid-state, except a very weak band at 8200 cm^{-1} in KNi(mnt). Therefore, these lowest-energy bands probably correspond to the intermolecular charge-transfer (CT) bands. Similar observations have been made on TCNQ anion radical salts[29] (TCNQ=tetracyanoquinodimethane); they have several electronic transitions from near-IR to visible region, among which the lowest-lying one or two peaks result from intermolecular CT transitions and higher-energy peaks correspond to the localized excitations within a single anion. In order to clarify the character of this band, the polarized optical measurements and photoconduction measurements are useful and now in progress.

IR Spectra. The frequencies of the bands observed in the IR spectra of KNi(mnt) and KPt(mnt) are given in Table 3, together with the assignments based on those of Schläpfer and Nakamoto.[14] A comparison of the IR spectra of both complexes indicates a surprising similarity.

As is well-known, IR spectra of the metal dithiolate complexes have following important features:

i) The frequencies of some modes, such as the C=C and C–S stretching modes, are dependent on the net charge of the [M(S$_2$C$_2$R$_2$)$_2$]^z molecule; when the complex is oxidized and then the net charge is decreased, the frequencies of the C=C and C–S modes decreases and increases, respectively. In other words, the HOMO of the monoanion is bonding with respect to the C=C bond but antibonding with respect to the C–S bond.

ii) In the case of the isolated molecule in solid state, such as in the dianion salts,[30] the dependence of the frequencies on the central metal M is very little, except for the M–S modes; the mass of the metal little affects the frequencies of modes arising principally from the ligand vibrations.

The most significant difference between KNi(mnt) and KPt(mnt) is that the band associated with the C=C modes in KPt(mnt) is much broad and energetically lower compared with the corresponding peak in KNi(mnt)(Fig. 4); the band of KPt(mnt) seems to comprise two C=C modes, whereas the band of KNi(mnt) is observed as a sharp single peak. In addition, the C–S mode of KPt(mnt) is seen at higher frequency than that of KNi(mnt)(see Table 3), which is consistent with the fact that the C=C modes of KPt(mnt) are observed at lower frequency than that of KNi(mnt).

These results can be interpreted as follows: Firstly, the lower shift in frequency of the C=C bands in KPt(mnt) than in KNi(mnt) results from the differences in the electron distribution within the whole anion; the electron density on the ligand in KPt(mnt) is smaller than that in KNi(mnt). Secondly, the broadening or splitting of the C=C bands in KPt(mnt) reflects a lower symmetry around the anion than in KNi(mnt), which suggests the dimerization of the anion stack. Although the electron density and symmetry mentioned above are complicatedly related to each other, it is probable that both of these two factors more or less affect the C=C modes of both two metal complexes.

Table 3. Observed IR Frequencies of KNi(mnt) and KPt(mnt) (cm^{-1})

KNi(mnt)	KPt(mnt)	Assignment
3628 m	3632 m	$\nu_3(H_2O)$
3552 vw	3558 vw	$\nu_1(H_2O)$
2208 s	2211 s	$\nu(C\equiv N)$
2196 sh	2200 sh	
1609 m	1607 m	$\nu_2(H_2O)$
1426 w	1422 ~1396 b	$\nu(C{=}C)$
1155 vs	1154 vs	$\nu(C{-}C)+\nu(C{-}S)$
1142 sh	1138 sh	?
1112 w	1108 w	$\pi(C{-}CN)$
1064 vw	1063 vw	$\nu(C{-}C)+\nu(C{-}S)$
869 vw	876 vw	$\nu(C{-}S)$

s: Strong, vs: very strong, m: medium w: weak, vw: very weak, b: broad, sh: shoulder.

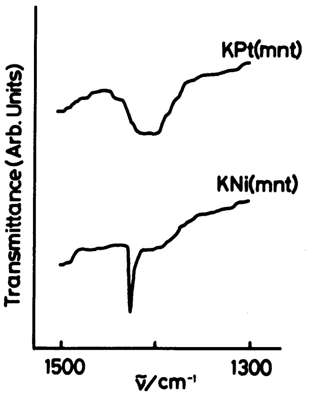

Fig. 4. The C=C stretching modes of KNi(mnt) (bottom curve) and KPt(mnt) (top curve). It can be pointed out that the C=C stretching modes around 1480 cm^{-1} which show the presence of the dianions are not observed for both complexes (see text).

Thermal Properties and Crystal Water. No anomalies can be detected in thermal analyses by DSC for both complexes except irreversible heat anomalies corresponding to the loss of crystal water. The loss of crystal water occured slightly higher in temperature (80—160 °C) in both complexes compared with the cases of $Li_{0.8}(H_3O)_{0.3}[Pt(mnt)_2]\cdot 1.7H_2O$ (50—133 °C)[8] or KCP(Br) (30—110 °C).[31] However, close inspection of the stretching and bending motions of crystal water indicates that the ν_1 and ν_3 modes occur at rather high frequencies for a solid[32] and the ν_2 mode occurs at a low frequency, which suggests that there are only weak hydrogen bondings in both complexes, similar in KCP(Br)(ν_1 or ν_3=3490 cm^{-1}).[33]

General Discussion. The measured thermal activation energies from the conductivity for both complexes would indicate 'band gaps' which are ca. 0.7 eV for KNi(mnt) and 0.36 eV for KPt(mnt). The electronic spectra, on the other hand, shows that the lowest-energy bands have peaks at higher energies, 0.93 eV (7500 cm^{-1}) for KNi(mnt) and 0.94 eV (7600 cm^{-1}) for KPt(mnt). This discrepancy indicates that the simple band model is not appropriate for the conduction mechanism and a hopping mechanism must be taken into account, as proposed by Ahmad et al. in the cases of $Rb[Pt(mnt)_2]\cdot 2H_2O$[19] and other dithiolate complexes.[26] Moreover, similar behaviors have been reported for alkali TCNQ salts, such as K(TCNQ).[29]

At this point, we must consider the polycrystalline nature of the samples; in this case grain boundary effects are not negligible. However, although it cannot be a priori determined whether the observed activation energies from the conductivity measurements correspond to the true values for the single-crystal samples or activation energies for electron hopping through the grain boundary, the 'band gaps' estimated from the conductivity data are lower than those from the solid-state spectra. Hence, it is certain that true band gaps for conduction, if any, are lower than the electronic band gaps; we can conclude that a hopping model is appropriate for the conduction mechanism. In the case of the hopping mechanism, repulsive Coulomb interactions are important in determining the conductivity behavior because the orbital for conduction is half-filled; the less Coulomb interactions lead to the higher conductivity.

On the basis of the hopping mechanism, we can understand the origin of the differences in the conductivity between KNi(mnt) and KPt(mnt). The IR spectra indicate a possibility that in KPt(mnt) the density of the unpaired electron on the ligand is lower than that of KNi(mnt). This possibility is also supported from the following consideration. In general, the metal d orbitals are raised in energy in the heavier transition metals, whereas the ligand-based orbitals are relatively unaffected. Although there is no detailed information about the mode of $[M(mnt)_2]^-$ stacking in both complexes, the structural similarities indicate that the ligand-dominant orbitals of both complexes are energetically equal. Following Schrauzer's MO scheme,[3,4,28] the HOMO of $[Ni(mnt)_2]^-$ monoanion salts is an antibonding combination of the ligand π and metal d_{xz} orbitals and the ligand π orbital associated with the HOMO lies energetically higher than the metal d orbital. The latter implies that the electron density is larger on the ligand (60%)[14] than on the metal. If one replaces Ni by a heavier atom Pt, the metal d orbitals rise in energy. As a result, one can expect larger mixing of the ligand π and metal d_{xz} orbitals compared with that in KNi(mnt), which leads lower density on the ligand in KPt(mnt). This lower density on the ligand of KPt(mnt) reduces the Coulomb interactions between anions, which facilitates higher conductivity. Although the differences in the electron distribution within the whole anion of both complexes may not be so large, this effect on the conduction arising from the hopping mechanism is possibly large.

In the above discussion, we have assumed that there is no contribution of structural difference between KNi(mnt) and KPt(mnt). In order to confirm whether or not above tentative explanation is true, further structural studies are necessary.

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