Optical and Magnetic Properties of $K[M\{S_2C_2(CN)_2\}_2]\cdot H_2O$ (M = Ni, Pt, or Au)

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The solid-state spectra of two series of $[M(mnt)_2]^-$$\{$mnt = $[S_2C_2(CN)_2]^{2-}$, M = Ni, Pt, or Au$\}$ monoanion salts of K^+ and $[NEt_4]^+$ have been recorded. The polarized absorption spectrum of $K[Ni(mnt)_2]\cdot H_2O$ is characterized by a strong band at 6 700 cm^{-1} assigned to the intermolecular charge-transfer (c.t.) transition along the stacking direction, which is the first direct evidence of the one-dimensional character of its electronic structure. On the contrary, the polarized reflectance spectra of $[NEt_4][M(mnt)_2]$ (M = Ni or Pt) are characterized by reflectance peaks at 7 200 cm^{-1}, corresponding to the intermolecular c.t. transition within the dimer. The magnetic susceptibilities of $K[M(mnt)_2]\cdot H_2O$ (M = Ni or Pt) are also described. The behaviour of the platinum complex can be explained by the alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain model with the alternation parameter $\alpha = 0.9$ and the exchange parameter $2|J| = 640$ cm^{-1}, which is consistent with its weakly dimerized stack structure.

Compounds of the type $M[M'(mnt)_2]$ [mnt = $S_2C_2(CN)_2{}^{2-}$; M = alkali metal; M′ = Ni, Pd, or Pt] have been prepared and some of them structurally characterized during the last ten years.[1–5] They contain a columnar structure in an eclipsed S-over-S configuration, which gives rise to anisotropic physical properties. In contrast with these salts of alkali-metal cations, well known salts of bulky organic cations (*e.g.* $[NEt_4]^+$) possess dimer pairs in a slipped configuration such that the central metal atom is positioned above the S atom of the other anion (*i.e.* metal over S configuration).[4,6] The influence of two types of arrangement of anions on their electronic structures is interesting in the context of the role of intermolecular and intramolecular interactions in determining the electronic properties.

Solid-state spectra and magnetic susceptibilities provide important information as regards the electronic structure. Nevertheless, very little work has been done on metal bis(mnt) complex salts; concerning the single-crystal spectra obtained with polarized light, only two examples have been reported so far and these involved the dianion salts $\{$*i.e.* $[NBu^n{}_4]_2[Ni(mnt)_2]$[7] and $[NMe_4]_2[Ni(mnt)_2]$[8]$\}$. Most reports on these complex salts have focused on their electrical conduction properties. In view of this fact, we have prepared $K[M(mnt)_2]\cdot H_2O$ (M = Ni, Pt, or Au) as examples of the first type of compounds mentioned above and measured their solid-state spectra and magnetic susceptibilities in order to investigate their electronic and magnetic properties. For comparison, we have also studied the electronic spectra of $[NEt_4][M(mnt)_2]$ (M = Ni, Pt, or Au) as examples of the second group.

Experimental

Preparation of Compounds.—Carbon, hydrogen, and nitrogen analyses were carried out by the Laboratory for Organic Elemental Microanalysis of Kyoto University.

The salts $K[M(mnt)_2]\cdot H_2O$ (M = Ni or Pt) were prepared as reported previously.[9] Single crystals of $K[Ni(mnt)_2]\cdot H_2O$ were obtained by slow evaporation of an acetone–water (1:4) solution of $K_2[Ni(mnt)_2]$ (0.2 mmol dm^{-3}) containing KCl (0.1 mmol dm^{-3}) and urea (0.1 mol dm^{-3}).

The salt $K[Au(mnt)_2]\cdot H_2O$ was prepared from $[NEt_4][Au(mnt)_2]$ (prepared according to the method of Davison *et al.*[10]). After filtration with Toyo GFP glass fibre filter paper to avoid contamination from colloidal Au, an acetone–water solution of $[NEt_4][Au(mnt)_2]$ (1×10^{-3} mol dm^{-3}) was passed through an ion-exchange column containing Dowex 50W × 8 in the acid form. The resulting solution of $H[Au(mnt)_2]$ was filtered as above, mixed with an aqueous solution of excess of KCl, and then evaporated. The reddish brown microcrystalline product was filtered off and washed with cold water. Elongated plate-like crystals of $K[Au(mnt)_2]\cdot H_2O$ are dichroic, orange-red and dark brown in polarized light parallel and perpendicular to the elongated direction, respectively, under a microscope (Found: C, 17.95; H, 0.45; Au, 37.00; K, 7.30; N, 10.35. Calc. for $C_8H_2AuKN_4OS_4$: C, 18.00; H, 0.40; Au, 36.85; K, 7.30; N, 10.50%). On the basis of oscillation and Weissenberg *X*-ray photographs, crystals of $K[Au(mnt)_2]\cdot H_2O$ were assigned to the Laue group *mmm* of the orthorhombic system. The systematic absences observed were $hk0$, $h = 2n + 1$ and $0kl$, $k + l = 2n + 1$, consistent with space groups $Pn2_1a$ or *Pnma*. The cell constants $a = 11.67$, $b = 29.16$, and $c = 4.04$ Å were determined from the *X*-ray powder diffraction pattern.

The salts $[NEt_4][M(mnt)_2]$ (M = Ni or Pt) were prepared according to the method of Davison and Holm.[11] Elongated plate-like crystals of $[NEt_4][Ni(mnt)_2]$ were grown by slow evaporation of its acetone–EtOH (4:1) solution (Found: C, 40.95; H, 4.25; N, 15.05. Calc. for $C_{16}H_{20}N_5NiS_4$: C, 40.95; H, 4.30; N, 14.90%). Elongated plate-like crystals of $[NEt_4][Pt(mnt)_2]$ were obtained similarly but using acetone–EtOH (3:1) as the solvent (Found: C, 31.70; H, 3.30; N, 11.60; S, 21.15. Calc. for $C_{16}H_{20}N_5PtS_4$: C, 31.75; H, 3.35; N, 11.55; S, 21.20%).

Physical Measurements.—*Solid-state spectra.* Solid-state spectra at room temperature (r.t.) and liquid-nitrogen temperature (77 K) were measured with a Jasco CT-100 spectrometer on single crystals or powdered samples dispersed in KBr pellets, using a tungsten lamp source. When necessary, a Gran-Thompson or Gran-Tayler prism was used for polarizing light. Samples were irradiated with the monochromatic light and a lock-in system working with HTV R376 and R316 photomultipliers and a PbS photoconductive cell for detection. Data were collected with a NEC 9801VX0 computer linked to

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Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, B.M. ≈ 9.27×10^{-24} J T^{-1}, G = 10^{-4} T, em mol^{-1} = $4\pi \times 10^{-6}$ m^3 mol^{-1}.

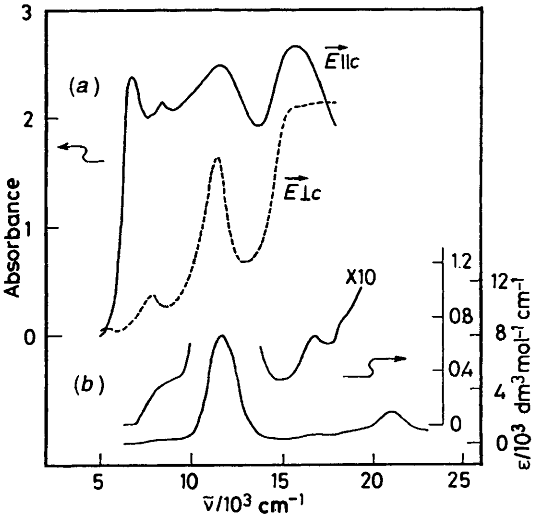

Figure 1. Electronic spectra of $K[Ni(mnt)_2]\cdot H_2O$: (*a*) polarized single-crystal absorption; (*b*) in acetonitrile solution at r.t.

Table 1. Electronic spectra (10^3 cm^{-1}) of $K[M(mnt)_2]\cdot H_2O$ (M = Ni or Pt)

	Single-crystal absorption (r.t.)		Powder absorption		
Compound	$\vec{E}\parallel c$	$\vec{E}\perp c$	r.t.	77 K	Solution[a]
$K[Ni(mnt)_2]\cdot H_2O$	6.7		7.3	7.5	
	8.4	7.8			8.2(2.4)
	11.7	11.3	10.8	11.0	11.6(3.9)
	15.8	15.2	15.1	15.5	16.7(2.8)
					18.7[b](2.9)
$K[Pt(mnt)_2]\cdot H_2O$			7.1	6.9 7.5	
			10.0	10.7	11.8(4.1)
			15.1	15.1	16.7(3.0)
					19.3(2.9)

[a] Acetonitrile; values in parentheses are log(ε/dm^3 mol^{-1} cm^{-1}). [b] Shoulder.

the lock-in amplifier. Details of this system were described elsewhere.[12]

Solution electronic spectra were measured on a Cary 17D spectrometer.

Single-crystal polarized reflectance spectra. Single-crystal polarized reflectance spectra at r.t. were obtained for the (110) face of $[NEt_4][Ni(mnt)_2]$ and (100) face of $[NEt_4][Pt(mnt)_2]$. The electric field vector ($\vec{E}$) was aligned both parallel and perpendicular to the needle axis (*c* axis) of the crystals. Only as-grown surfaces were measured and typical sample dimensions of both compounds were 4 × 2 × 0.4 mm. Absolute reflectivities were calibrated with an aluminium mirror.

Magnetic susceptibility. Magnetic susceptibilities for polycrystalline samples were measured using a SHE VTS-905 SQUID susceptometer at the external magnetic field of 19.5 kG. Sample holders made of Al–Si were employed. The background was obtained over the full temperature range prior to measuring the samples. Sample amounts varied from 100 to 200 mg. In order to exclude the paramagnetic oxygen gas, the sample space was evacuated by a rotary pump and then filled by helium gas [*ca.* 760 mmHg (*ca.* 10^5 Pa) at r.t.]. After this procedure was repeated two more times, the samples were rapidly cooled to 4 K to minimize loss of the water of crystallization. The data were taken on warming the sample from 4 K in a helium-gas atmosphere.

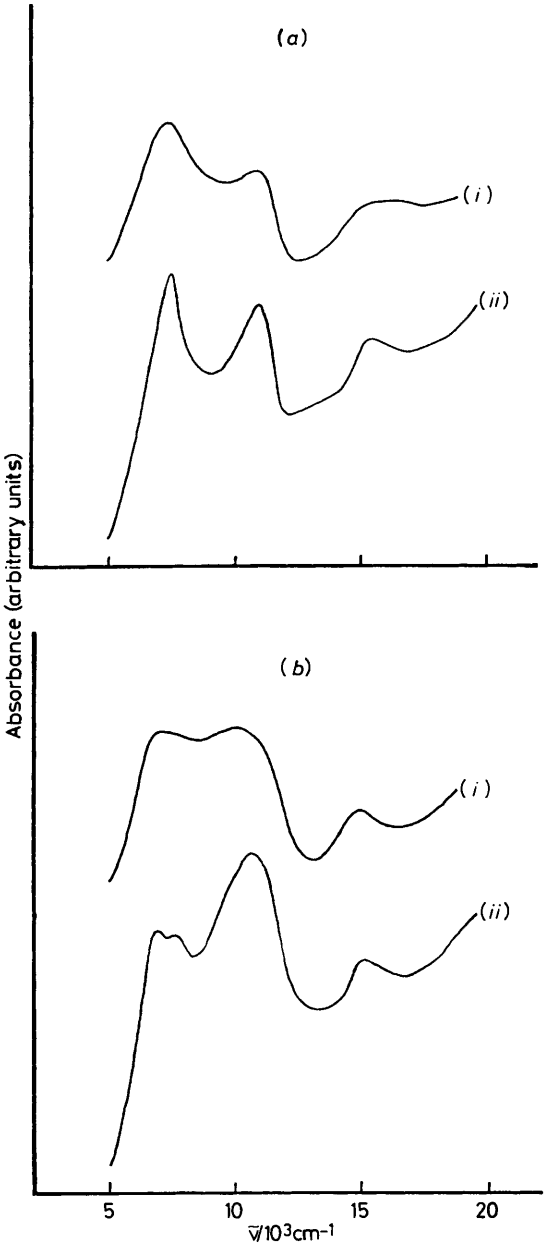

Figure 2. Absorption spectra of (*a*) $K[Ni(mnt)_2]\cdot H_2O$ and (*b*) $K[Pt(mnt)_2]\cdot H_2O$ in KBr pellets at (*i*) r.t. (*ca.* 290 K) and (*ii*) 77 K

Results and Discussion

Optical Spectra of $K[Ni(mnt)_2]\cdot H_2O$.—Figure 1 shows the single-crystal polarized absorption spectra at r.t., together with solution spectra in acetonitrile. The peak positions are listed in Table 1. The spectra were measured with the electric field vector $\vec{E}$ parallel and perpendicular to the stacking direction (*c* axis).

The main feature is that, only for $\vec{E}\parallel c$, is a strong absorption band at 6 700 cm^{-1} observed. This band can be assigned to the intermolecular charge-transfer (c.t.) transition along the stacking direction, which indicates a strong π–π interaction due to a columnar structure; this is direct evidence that the electronic structure of $K[Ni(mnt)_2]\cdot H_2O$ has one-dimensional character.

On the other hand, the $\vec{E}\perp c$ absorptions at 7 800 and 11 300 cm^{-1} are similar to those observed in acetonitrile solution but slightly (about 300 cm^{-1}) shifted to lower energy. These can be

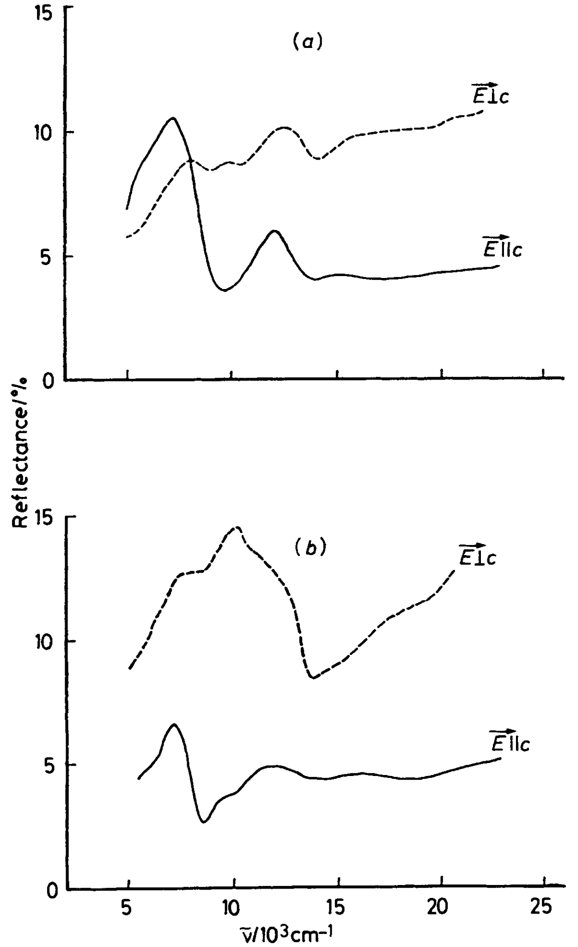

Figure 3. Polarized reflectance spectra of (*a*) $[NEt_4][Ni(mnt)_2]$ and (*b*) $[NEt_4][Pt(mnt)_2]$ at r.t.

assigned to in-plane intramolecular transitions.* For $\vec{E}\| c$, similar absorption bands at 8 400 and 11 700 cm^{-1}, slightly shifted to higher energy, are observed. These also can be assigned to in-plane transitions; they can be observed for $\vec{E}\| c$ because the $[Ni(mnt)_2]^-$ anion planes are tilted with respect to the *c* axis {for $[NH_4][Ni(mnt)_2]\cdot H_2O$, which is isomorphous with the potassium salt,[9] this tilting angle is [3] 26.2°}.

Temperature Dependence of the Powder Absorption Spectra of $K[M(mnt)_2]\cdot H_2O$ (M = Ni *or* Pt).—Results are shown in Figure 2 and Table 1. For both complexes the lowest-energy bands in the solid-state spectra, which are absent in solution, have been attributed to intermolecular c.t. transitions.[9] The spectra of the nickel complex at r.t. and 77 K are very similar. In the case of the platinum complex the intermolecular c.t. transition at 7 100 cm^{-1} at r.t. splits into two bands at 6 900 and 7 500 cm^{-1} at 77 K. This suggests dimerization of the $[Pt(mnt)_2]^-$ chain along the *c* axis. However, the magnetic susceptibility data show no transition between 10 and 300 K (see below). Therefore, we conclude that this dimerization is already present at r.t. and that the apparent single absorption band is observed owing to thermal broadening.

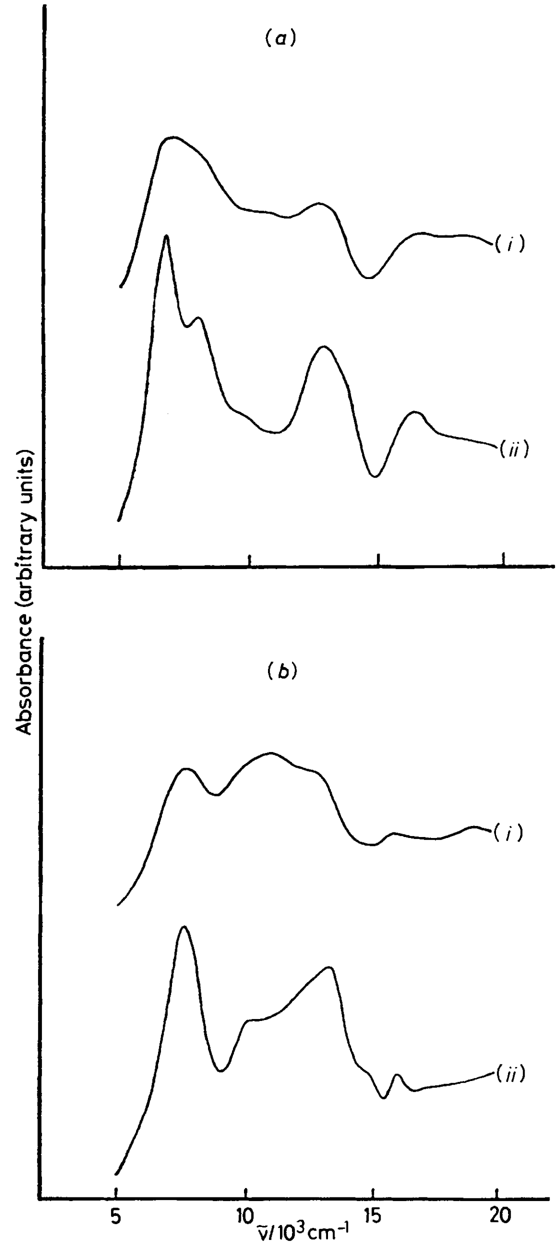

Figure 4. Absorption spectra of (*a*) $[NEt_4][Ni(mnt)_2]$ and (*b*) $[NEt_4][Pt(mnt)_2]$ in KBr pellets at (*i*) r.t. (*ca.* 290 K) and (*ii*) 77 K

Optical Spectra of $[NEt_4][M(mnt)_2]$ (M = Ni *or* Pt).—Results are shown in Figures 3 and 4, and Table 2.

We will focus attention on the near-i.r. region. In Figure 3 the lowest-energy $\vec{E}\| c$ reflectance peaks at 7 200 cm^{-1} for both complexes are ascribed to the intermolecular c.t. transitions within the dimer along the stacking direction (*c* axis). This is quite natural considering that the $[NEt_4]^+$ salts possess dimer pairs[4,6] and their interdimer interactions are very weak according to their magnetic susceptibilities reported by Weiher *et al.*;[15] they treated both salts as a system of isolated dimers within which the antiferromagnetic interaction with $S = \frac{1}{2}$ is present.

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* Although there have been several attempts to assign the solution spectra, some controversy still exists; according to Gray and co-workers,[13] these two peaks are assigned to $d_{xz} \longrightarrow d_{x^2-y^2}$ and ligand $\pi \longrightarrow d_{x^2-y^2}$ respectively while they are assigned to $d_{x^2-y^2}, d_{yz}, d_{z^2} \longrightarrow$ ligand $\pi(+d_{xz})$, and ligand $\pi \longrightarrow$ ligand $\pi(+d_{xz})$ respectively by Schrauzer and Mayweg.[14] In this description, all the atoms in $[Ni(mnt)_2]^-$ are put on the *xy* plane, and the *x* axis is placed so as to correspond with the long axis of the molecule.

Table 2. Electronic spectra (10^3 cm^{-1}) of $[NEt_4][M(mnt)_2]$ (M = Ni or Pt)

Compound	Powder absorption		Single-crystal reflectance		
	r.t.	77 K	$\vec{E}\parallel c$	$\vec{E}\perp c$	Solution[a]
$[NEt_4][Ni(mnt)_2]$	7.1	6.8	7.2		
	8.3[b]	7.9		8.0	8.2(2.4)
	10.8[b]	10.0[b]		9.9	11.6(3.9)
	12.7	12.9	12.1	12.5	
	16.7	16.4	15.2	15.7[b]	16.7(2.8)
					18.7[b](2.9)
$[NEt_4][Pt(mnt)_2]$	7.6	7.6	7.2	7.4[b]	
	10.8	10.2	9.3[b]	10.1	11.8(4.1)
	13.0[b]	13.3	12.0	13.0[b]	
		14.8[b]			
	15.8	16.0	16.2	17.5[b]	16.7(3.0)
					19.3(2.9)

[a] Acetonitrile; values in parentheses are log(ε/dm^3 mol^{-1} cm^{-1}). [b] Shoulder.

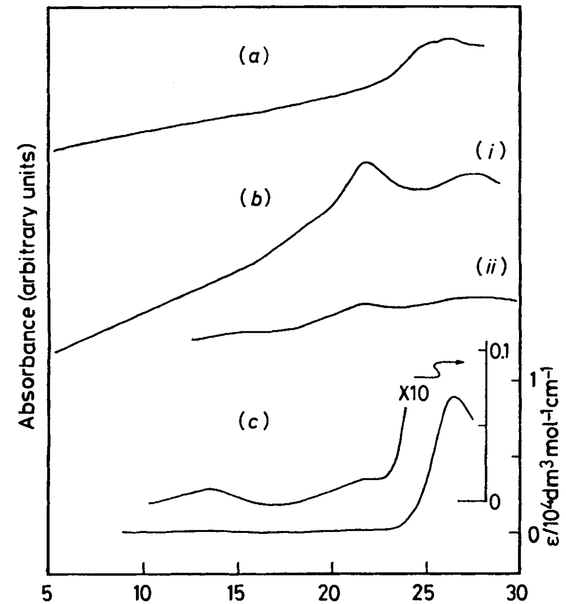

Figure 5. Absorption spectra of (*a*) $[NEt_4][Au(mnt)_2]$ in a KBr pellet at r.t., (*b*) $K[Au(mnt)_2]\cdot H_2O$ in a KBr pellet at (*i*) r.t. and (*ii*) 77 K, and (*c*) in acetone–water (1 : 1) at r.t.

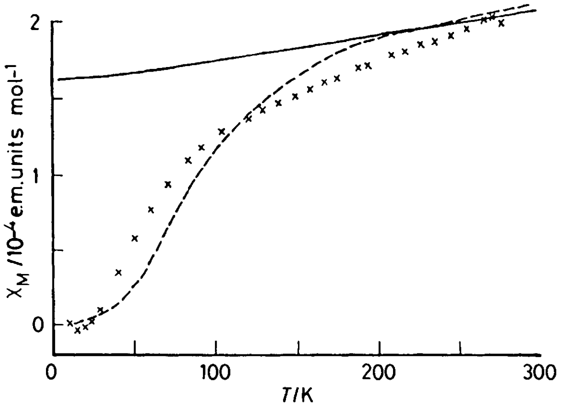

Figure 6. Temperature dependence of the molar magnetic susceptibility of $K[Ni(mnt)_2]\cdot H_2O$. The magnetic susceptibilities calculated from the theory of an alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain with $2|J| = 710$ cm^{-1}, $\alpha = 1$ and 0.9, and $g = 2$ are shown as the solid ($\alpha = 1$) and broken ($\alpha = 0.9$) curves respectively.

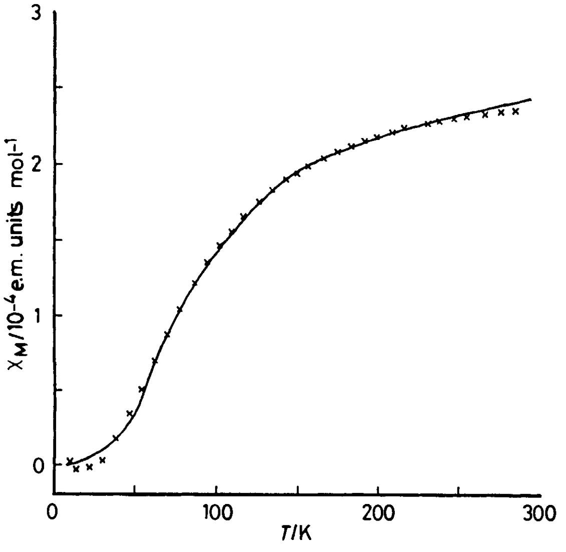

Figure 7. Temperature dependence of the molar magnetic susceptibility of $K[Pt(mnt)_2]\cdot H_2O$. The magnetic susceptibility calculated from the theory of an alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain with $2|J| = 640$ cm^{-1}, $\alpha = 0.9$, and $g = 2.08$ is shown as the solid curve

Optical Spectra of $[NEt_4][Au(mnt)_2]$ *and* $K[Au(mnt)_2]\cdot H_2O$.—Results are shown in Figure 5. Unlike $K[M(mnt)_2]\cdot H_2O$ (M = Ni or Pt), the solid-state absorption spectrum of $K[Au(mnt)_2]\cdot H_2O$ is characterized by no distinct absorption band between 5 000 and 15 000 cm^{-1}. On the other hand, a strong band at 21 800 cm^{-1} is observed at both r.t. and 77 K, which is not present in the solution spectra and in the spectra of the $[NEt_4]^+$ salt. The potassium salt is isomorphous with its nickel analogue[9] while the $[NEt_4]^+$ salt seems to be isomorphous with $[NEt_4][M(mnt)_2]$ (M = Ni or Pt)[4,6] according to its *X*-ray powder diffraction pattern. Therefore, the band at 21 800 cm^{-1} of the potassium salt can be ascribed to the intermolecular c.t. transition along the stacking direction (*c* axis) and is characteristic of π–π interaction in eclipsed S-over-S configuration; this band corresponds to the bands around 7 000 cm^{-1} of its nickel and platinum analogues (see Figures 1 and 2), but a large blue shift from these bands is observed for the gold complex. This is because the former transition is a h.o.m.o. ⟶ h.o.m.o. transition while the highest occupied molecular orbital (h.o.m.o.) of the latter is fully occupied and the corresponding transition is a h.o.m.o. ⟶ l.u.m.o. (lowest unoccupied molecular orbital) transition. On the other hand, the corresponding transition is not observed for the $[NEt_4]^+$ salt. This is perhaps because the interaction within the dimer, if present, is very weak.

Magnetic Properties of $K[M(mnt)_2]\cdot H_2O$ (M = Ni *or* Pt).—Figures 6 and 7 show the molar magnetic susceptibilities of $K[Ni(mnt)_2]\cdot H_2O$ and $K[Pt(mnt)_2]\cdot H_2O$, respectively. For both salts the low-temperature data ($T < 30$ K) can be fitted by $\chi = \chi_0 + C/T$ which has been subtracted* in Figures 6 and 7.

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* Nevertheless, unlike $[NH_4][Ni(mnt)_2]\cdot H_2O$,[16,17] the constant χ_0 terms for both the nickel and platinum complex salts disagree with the core diamagnetism $\chi_M{}^d$ calculated from Pascal's constants; although this calculation procedure has some uncertainty, the calculated values are 154×10^{-6} e.m. units mol^{-1} for the nickel and 182×10^{-6} e.m. units mol^{-1} for the platinum complex (see also Table 3). Whether this disagreement is due to the existence of temperature-independent paramagnetism, $\chi_{t.i.p.}$, or not remains uncertain.

Table 3. Antiferromagnetic interaction parameters[a] for $[M(mnt)_2]^-$ monoanion salts (M = Ni, Pd, or Pt)

Compound	$\mu_{r.t.}$/B.M.	$2\|J\|$/cm^{-1}	α	$-(\chi_M{}^d + \chi_{t.i.p.})$/10^{-4} e.m. units mol^{-1}	Ref.
$[NEt_4][Ni(mnt)_2]$	0.96	620	0	2.6	15
$[NEt_4][Pd(mnt)_2]$	Dia.	>1 000	—	—	15
$[NEt_4][Pt(mnt)_2]$	1.15	350	0	2.2	15
$[NH_4][Ni(mnt)_2]\cdot H_2O$	0.93	420 (>200 K)	1	1.34	16
α-$[NH_4][Ni(mnt)_2]\cdot H_2O$	*b*	80 (>200 K)	1	*b*	17
β-$[NH_4][Ni(mnt)_2]\cdot H_2O$	*b*	160	0	*b*	17
$K[Ni(mnt)_2]\cdot H_2O$	0.7	>710	?	0.17	This work
$K[Pt(mnt)_2]\cdot H_2O$	0.7	640	0.9	0.99	This work
$Cs[Ni(mnt)_2]\cdot H_2O$	1.36	270	0	*b*	17

[a] Alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain model; α = alternation parameter. [b] Not reported.

From this C/T term, the estimated $S = \frac{1}{2}$ impurity concentrations were 2.6% for the nickel and 1.9% for the platinum complex.

First, the room-temperature magnetic moments are *ca.* 0.7 B.M. for both salts, strongly reduced from the expected spin-only moment of 1.73 B.M. Secondly, for both salts, there is a decrease in the susceptibility and hence in the magnetic moment with decreasing temperature, indicative of antiferromagnetic intermolecular interactions.

For the platinum complex the susceptibility data can be described reasonably well by the theory of the alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain. The exchange Hamiltonian for this can be written as in equation (1),[18] where J

$$H = -2J\sum_i (S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1}) \qquad (1)$$

is the exchange parameter ($J < 0$) and α is the alternation parameter which shows the degree of alternation of the antiferromagnetic interactions ($0 \leqslant \alpha \leqslant 1$; when $\alpha = 0$ the model is reduced to the dimer model with pairwise interaction, and when $\alpha = 1$ the model becomes the uniform linear-chain model). The corresponding curves of susceptibility *vs.* temperature have been numerically calculated by Bonner *et al.*[18] for various alternation parameters. The solid line in Figure 7 is generated with the best-fit parameters $\alpha = 0.9$, $2|J| = 640$ cm^{-1}, and $g = 2.08$ in this model.

On the other hand, the magnetic susceptibility of the nickel analogue was not satisfactorily described by the same model; attempts to fit the susceptibility data near 300 K with the above model, using $\alpha = 0.9$ or 1.0 and setting $g = 2$, are also shown in Figure 6. A value of $2|J| \approx 710$ cm^{-1} was obtained from this fitting. Of course, this is a rough estimation of the magnitude of the antiferromagnetic interactions in this nickel complex salt.

Furthermore, a closer look at Figure 6 shows that the susceptibility curve has an inflection around 80 K, from which temperature $\chi(T)$ rapidly decreases and goes to zero around 20 K. This suggests the existence of a phase transition around 50 K, around which the dimerization probably occurs. However, in order to clarify this, further investigation is necessary.

General Discussion.—The one-dimensional nature of the electronic structure of $K[Ni(mnt)_2]\cdot H_2O$, which is shown by the single-crystal absorption spectra, is related to its stack structure. Thus, the electronic structure of the platinum analogue probably reflects its similar crystal structure.[9] In $[NH_4][Ni(mnt)_2]\cdot H_2O$, which is isomorphous with $K[Ni(mnt)_2]\cdot H_2O$,[3,9] the arrangement of the planar $[Ni(mnt)_2]^-$ anions in the stacks forms a two-dimensional sheet network *via* interstack side-by-side S $\cdots$ S contacts observed previously in other mnt complex salts,[2,19] but within these anionic sheets neighbouring stacks are displaced vertically from each other by half an intrastack S $\cdots$ S distance, suggesting very little two-dimensional character.[3] Our result is consistent with this structural feature.

Next, we will consider the magnetic properties of the metal bis(mnt) complex salts. So far there have been two reports on the magnetic susceptibilities of these complex salts of small cations such as those of the alkali metals. They are listed in Table 3, together with the data for $[NEt_4]^+$ salts from Weiher *et al.*[15] The behaviour of $\chi(T)$ for $K[Pt(mnt)_2]\cdot H_2O$ is consistent with its weakly dimerized stack structure, suggested by the i.r. spectrum[9] and the electronic spectrum at 77 K. Nevertheless, the temperature dependence of $\chi(T)$ for its nickel analogue, $K[Ni(mnt)_2]\cdot H_2O$, is not understood; the structural[9] and optical results show that it possesses an equidistant stack structure like that of $[NH_4]^+$ salt;[3] thus this salt is expected to behave like an antiferromagnetic Heisenberg chain model at least around r.t. The $[NH_4]^+$ salt has been shown to behave like this.[16,17] However, there have been several reports that compounds such as $Cs_2[tcnq]_3$[20] (tcnq = tetracyanoquinodimethene) and hexamethylenetetrathiafulvalene–tetrafluorotetracyanoquinodimethane[21] possessing the equidistant stack structure in the high-temperature phase do not behave like a one-dimensional Heisenberg antiferromagnet; $\chi(T)$ of these compounds decreases more rapidly with decreasing temperature than predicted from the above theoretical model. In other words, an increasing J value with decreasing temperature has been observed. In this case it is believed that the long-range Coulomb interactions which are neglected in the above model play an important role in determining $\chi(T)$. This interpretation is probably true of our case but it remains unknown what distinguishes $K[Ni(mnt)_2]\cdot H_2O$ from $K[Pt(mnt)_2]\cdot H_2O$ and $[NH_4][Ni(mnt)_2]\cdot H_2O$, the last two following the alternating antiferromagnetic Heisenberg chain model.

Finally, we will try to extract quantitative information from the optical and magnetic results obtained. In the $[M(mnt)_2]^-$ (M = Ni or Pt) monoanion salts the h.o.m.o. is the half-filled orbital, which forms a half-filled band. In this case, the on-site Coulomb repulsion U between two electrons on the same molecule becomes important. Thus, we recall the Hubbard model as one appropriate model to describe the nature of the electronic properties of this system. As is well known, this model only includes the on-site Coulomb repulsion U and the electron-transfer energy t, the latter being related to the electronic band width W by $W = 4t$; the long-range Coulomb interactions are neglected in this model. Except for $K[Pt(mnt)_2]\cdot H_2O$ ($\sigma_{r.t.} = 10^{-1}$ S cm^{-1} for single crystals parallel to the stacking direction[22]), the remaining three salts, $K[Ni(mnt)_2]\cdot H_2O$[9,23] and $[NEt_4][M(mnt)_2]$ (M = Ni or Pt),[24] have low conductivities ($\sigma_{r.t.} \lesssim 10^{-6}$ S cm^{-1}). Therefore, the relation $U \gg 4t$, where the unpaired electron is expected to be localized on each molecule, seems a suitable condition as a starting point. In this extreme limit, the spin-dependent part of the Hubbard Hamiltonian can be written as the Heisenberg Hamiltonian with an antiferromagnetic exchange parameter $J(<0)$ given by $2|J| = 4t^2/U$. Note that the $\chi(T)$ values of three complex salts, $K[Pt(mnt)_2]\cdot H_2O$ and $[NEt_4][M(mnt)_2]$ (M = Ni or Pt),[15] are like those of an alternating antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain model.

Like alkali-metal tcnq salts,[25,26] one approximate measure of U for this system can be obtained from the intermolecular c.t. band along the $[M(mnt)_2]^-$ stack. We obtained $U = 0.9$ eV for all four salts. Using the magnitude of J and the relation $2|J| = 4t^2/U$, the estimated values of $4t$ are 0.8 eV for two potassium salts, 0.7 eV for $[NEt_4][Ni(mnt)_2]$, and 0.6 eV for $[NEt_4][Pt(mnt)_2]$. Although, these sets of estimates for U and $4t$ do not fall in the region of $U \gg 4t$, we can get some insight into the nature of their electronic structure as shown below.

The main feature is that the sets of U and $4t$ obtained are little dependent on the central metal or the type of arrangement of the $[M(mnt)_2]^-$ anions. This is striking because the magnetic and conductivity behaviours of these salts are often quite sensitive to their central metal and, of course, to the types of arrangement of the anions. The parameter t is characterized by the intermolecular interactions *via* S $\cdots$ S or S $\cdots$ M contacts. On the other hand, U is mainly related to the electron delocalization within the molecule. Therefore, the above-mentioned similarity in the sets of U and $4t$ means that the degree of delocalization of the lone-pair electron in the anion is almost equal in the nickel and platinum complexes and that the two types of intermolecular interactions, S $\cdots$ S and S $\cdots$ M, make little difference. Here, the parameter t for the metal over S configuration is concerned with the intradimer interaction which includes the central metal. Values of t obtained for the two $[NEt_4]^+$ salts seem to reflect the difference in the central metal. In view of the crudeness of this estimation for U and $4t$, however, it is uncertain that the difference in $4t$ for the two salts is meaningful.

It is instructive to compare these metal bis(mnt) complex salts with other compounds in which the Hubbard-type intersite transition is observed. There have been two different types of examples. First α-$TiCl_3$,[27] which is a *d*-band material, U being estimated to be 2—3 eV from its optical spectra. Secondly are alkali-metal tcnq salts,[26] which have strong π–π interactions along the stacking direction, U being estimated to be *ca.* 1 eV. At a glance, the metal bis(mnt) complex salts seem to occupy a middle position between the above two groups in that they have both transition-metal *d* orbitals and a ligand π system. However, this system is similar in nature to the second group, considering that the effect of the central metal on the electronic properties is largely 'diluted' by the large admixture of the metal *d* orbitals and ligand π system and that the π system plays a dominant role in determining their electronic structures. In order to understand the subtle but never negligible effects of the central metal ions of the metal bis(mnt) complex salts on their electronic properties a more complicated model is necessary.

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