Electrical Conduction and Electron Spin Resonance Studies on the Mixed Crystals of $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$[‡]

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An attempt to control the electronic properties of the bis(mnt) metal complex salt system through use of mixed crystals has been examined (mnt = maleonitriledithiolate). The $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$ series has been investigated as the 'modification' of the central metal. An almost two orders of magnitude higher conductivity was observed for samples having $x = 0.04$ compared with $x = 0$. From ESR measurements, a pronounced reduction in g anisotropy for $x = 0.04$ suggests that the excess of conductivity for $x = 0.04$ may be attributed to the presence of mobile carriers in the defect states.

The electronic properties of transition-metal bis(dithiolene) complexes can be varied by changes in the central metal, the ligand substituent and the donor molecules. Among these three factors of structural modification, we have focused on the role of the central metal in the electrical conduction and searched for the possibility of controlling it by 'modification' of the central metal.

We chose the bis(mnt) complexes (mnt = moleonitriledithiolate = 1,2-dicyano-1,2-ethylenedithiolate) and prepared the series $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$ as the 'modification' of the central metal. A similar approach has been used with organic molecular solids such as $(ttf)_{1-x}(tsf)_x(tcnq)$[1] [ttf = tetrathiafulvalene = 2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole; tsf = tetraselenium analogue; tcnq = tetracyanoquinodimethane] or $(mphenz)_{1-x}(phenz)_x(tcnq)$[2] (phenz = phenazine, mphenz = *N*-methylphenazinium). In the latter study, Miller and Epstein clearly pointed out that control of the band filling is achieved with (mphenz)(tcnq) by partial replacement of mphenz cations with neutral phenz molecules. In our approach, this partial replacement is done with bis(mnt) complex anions containing a different central metal, *i.e.* $[Pt(mnt)_2]^-$ stack is partially replaced by $[Au(mnt)_2]^-$; because of its similar size and shape, $[Au(mnt)_2]^-$ is able to crystallize with $[Pt(mnt)_2]^-$. On the other hand, $[Pt(mnt)_2]^-$ and $[Au(mnt)_2]^-$ have different oxidation states of the ligand; the highest occupied molecular orbital (HOMO) of the former is half filled while in the latter it is fully occupied. Therefore, we could expect that the mixed crystal has mixed oxidation states of the mnt ligand. This is the first example of 'modification' of the central metal in a metal bis(mnt) complex salt system and of studying its related effect on the electronic properties.

Experimental

Preparation.—The salts $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$ were grown by slow evaporation of acidic (pH 1, using HCl) acetone–water (3:1) solution containing $K[Pt(mnt)_2]\cdot H_2O$ and $K[Au(mnt)_2]\cdot H_2O$; the last two compounds were prepared as reported previously.[3,4] The crystals obtained are elongated plate-like and have a typical size of 1.5 × 0.1 × 0.01 mm. Their molar ratios of Au, x, were determined by atomic absorption analysis. For initial concentrations $x = 0.07$ and $x = 0.11$ in the mixture, crystals with composition $x = 0.04 \pm 0.01$ and $x = 0.08 \pm 0.01$ respectively, were obtained. Elemental analysis results (for C, H and N; Laboratory for Organic Elemental Microanalysis of Kyoto University) for polycrystalline samples of all three compounds were consistent with the formula $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$; $K[Pt(mnt)_2]\cdot H_2O$, (Found: C, 18.00; H, 0.40; K, 7.0; N, 10.20; H_2O, 3.45. Calc. for $C_8H_2KN_4OS_4$: C, 18.05; H, 0.40; K, 7.35; N, 10.50; H_2O, 3.50%), $K[Pt_{0.96}Au_{0.04}(mnt)_2]\cdot H_2O$ (Found: C, 18.60; H, 0.50; Au, 1.4; K, 6.6; N, 10.30. Calc. for $C_8H_2Au_{0.04}KN_4OPt_{0.96}S_4$: C, 18.05; H, 0.40; Au, 1.50; K, 7.35; N, 10.50%), and $K[Pt_{0.92}Au_{0.08}(mnt)_2]\cdot H_2O$ (Found: C, 18.80; H, 0.50; Au, 2.6; K, 7.1; N, 10.60. Calc. for $C_8H_2Au_{0.08}KN_4OPt_{0.92}S_4$: C, 18.05; H, 0.40; Au, 3.00; K, 7.35; N, 10.50%).

Measurements.—Powder X-ray diffraction studies showed that there are no Au^0 and $K[Au(mnt)_2]\cdot H_2O$ contaminations in these systems. The IR spectra indicated that the mixed crystals contain $[Pt(mnt)_2]^-$ and $[Au(mnt)_2]^-$. Lattice constants at room temperature were measured by using oscillation and Weissenberg photographs and the overall crystal structure of $K[Pt(mnt)_2]\cdot H_2O$ remains unchanged for $0 \leqslant x \leqslant 0.08$.

Electrical conductivity measurements were performed on single crystals along the needle axis (*c* axis, *i.e.* stacking direction) using a two-probe d.c. technique; two gold wires, one for the current lead and the other for the voltage measurements, were attached to each end of the crystal using gold paint. The measurements under pressure were made using a beryllium–copper-clamped cell with spindle oil as the pressure medium.

The ESR spectra of the polycrystalline samples were obtained on a JEOL PE-3X X-band spectrometer using 100 kHz field modulation. Variable temperatures from 3.7 K to room temperature were provided by a flowing-gas cryostat system (Oxford Instruments ESR-900). The temperature of the sample was measured by a AuFe-normal silver thermocouple positioned near the sample. Stability was better than ±2 K. Calibration of g values was based on dpph (diphenylpicrylhydrazyl, $g = 2.0036$) and Mn^{2+}-doped MgO single crystals.

Results and Discussion

The temperature dependence of needle-axis conductivities for samples of composition $x = 0$, 0.04 and 0.08 is shown in Fig. 1. The absolute values of the room-temperature conductivities $\sigma_{r.t.}$ and the activation energies E_a obtained by using the relation $\sigma = \sigma_0\exp(-E_a/k_BT)$ are given in Table 1. The conductivity was measured for several crystals of each composition. The results for crystals from the same batch were reproducible within the small variation given in Table 1. All three samples exhibit thermally activated semiconducting behaviour at all temperatures. However, for $x = 0.04$, an almost two orders of

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[‡] *Non-SI units employed:* eV ≈ 1.60×10^{-19} J, G = 10^{-4} T.

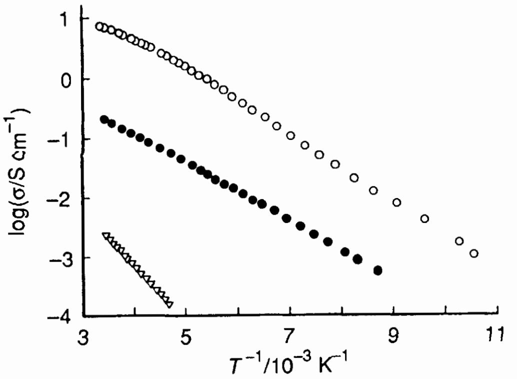

Fig. 1 Temperature dependence of the c-axis electrical conductivities of $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$: x = 0 (●), 0.04 (○) and 0.08 (▽)

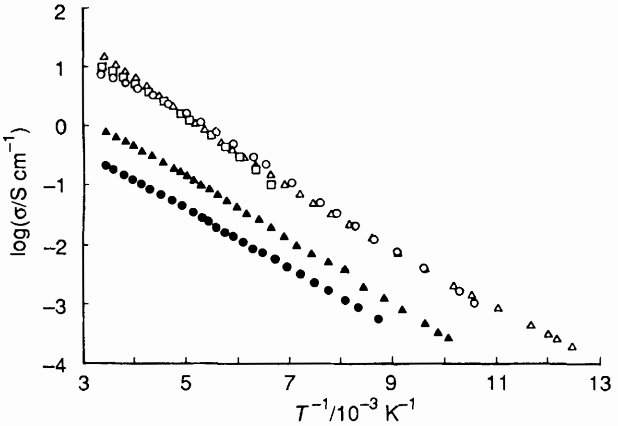

Fig. 2 Temperature dependence of the c-axis conductivities of $K[Pt_{0.96}Au_{0.04}(mnt)_2]\cdot H_2O$ at ambient pressure (○), 0.22 GPa (□) and 0.96 GPa (△) and $K[Pt(mnt)_2]\cdot H_2O$ at ambient pressure (●) and 0.93 GPa (▲)

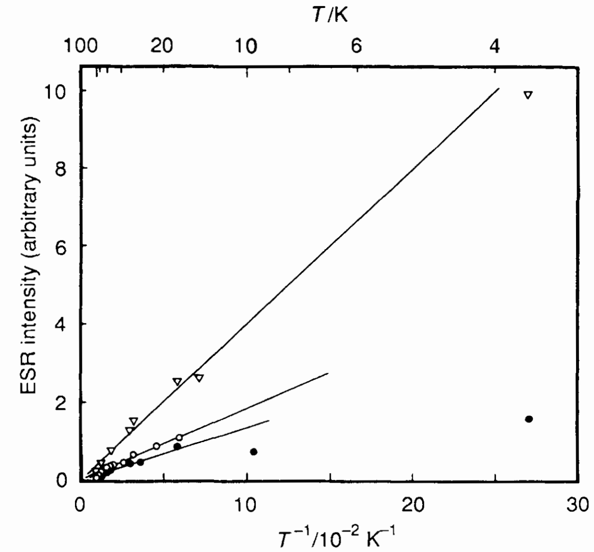

Fig. 3 Temperature dependence of the ESR signal intensity for polycrystalline $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$: x = 0 (●), 0.04 (○) and 0.08 (▽). These signal intensities are corrected so that they are proportional to the concentrations of their Curie-like spins.

magnitude higher conductivity was observed compared with the sample for which $x = 0$. On the other hand, the sample having $x = 0.08$ showed lower conductivity with larger E_a than those of the other two.

The conductivity measurements were also made under pressure. Fig. 2 shows the conductivities of the samples for which $x = 0$ and $x = 0.04$ as a function of temperature under

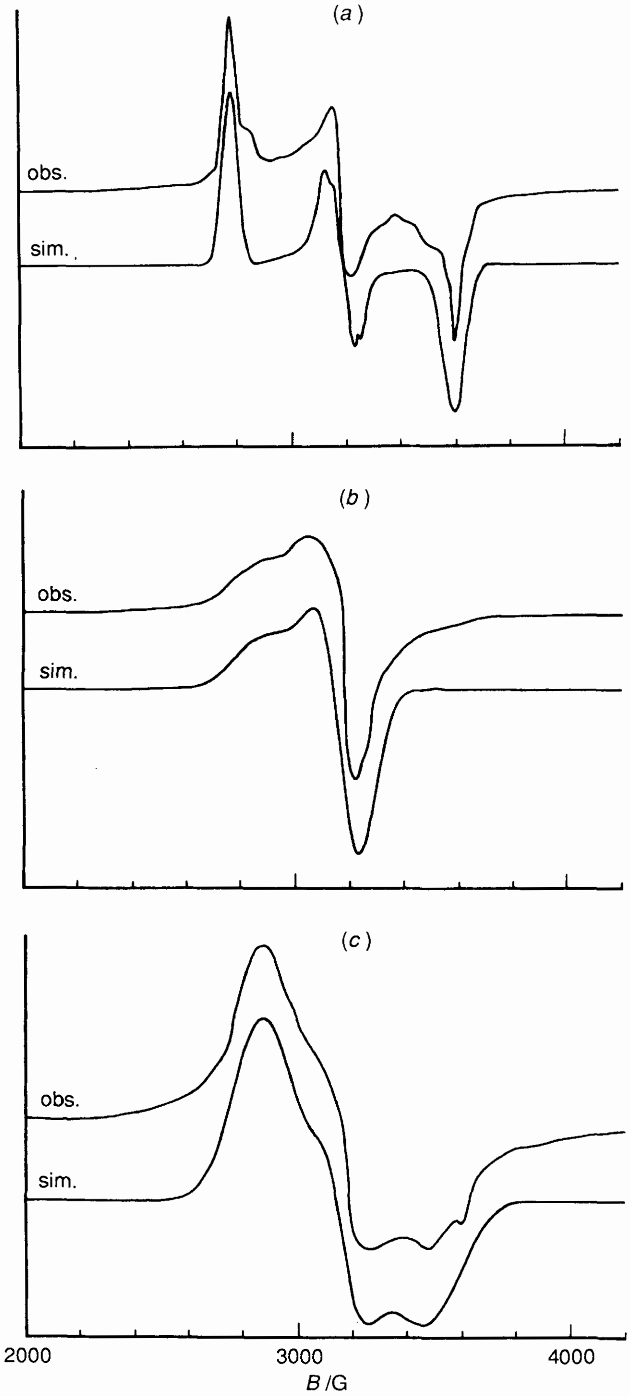

Fig. 4 Powder ESR spectra of (a) $K[Pt(mnt)_2]\cdot H_2O$, (b) $K[Pt_{0.96}Au_{0.04}(mnt)_2]\cdot H_2O$ and (c) $K[Pt_{0.92}Au_{0.08}(mnt)_2]\cdot H_2O$ at 17 K. Simulated (sim.) spectra were obtained by using the spin-Hamiltonian parameters listed in Table 2.

Table 1 Room-temperature (r.t.) conductivities and activation energies around r.t. for various compositions of $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$

x	$\sigma_{r.t.}$/S cm^{-1}	E_a(r.t.)/meV
0	0.16–0.20*	*ca.* 85
0.04	4–7*	*ca.* 60
0.08	2.3×10^{-3}–2.5×10^{-4}*	*ca.* 190

* Range for samples examined

Table 2 ESR parameters for $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$ at 17 K

					Linewidth[a]/G			Hyperfine tensor[b]/G			
x	g_1	g_2	g_3	$<g>$	H_1	H_2	H_3	A_1	A_2	A_3	$<A>$
0	2.348	2.051	1.814	2.07	55	53	80	*ca.* 0	100	*ca.* 0	33
0.04	2.27	2.0583	2.0580	2.13	170	140	140	150	70	70	97
0.08	2.27	2.06	1.87	2.07	190	130	175	150	100	200	150
Magnetically diluted $[Pt(mnt)_2]^-$[c]											
	2.245	2.065	1.827	2.04				0	130	116	82

[a] Peak-to-peak linewidth. [b] ^{195}Pt (nuclear spin $I = \frac{1}{2}$, natural abundance 33.7%) splittings. [c] Ref. 5.

pressure. When the pressure increases both inter- and intramolecular distances between adjacent atoms decrease. In molecular solids the former effect is usually dominant for the conductivity under relatively low pressure (a few GPa). Hence, increasing pressure increases $\sigma_{r.t.}$ but decreases E_a. Our results, however, are anomalous; for the sample having $x = 0$ the pressure increases $\sigma_{r.t.}$ as expected but gives no change in the E_a. On the other hand, the pressure has little influence on the conductivity and E_a for $x = 0.04$ except in the room-temperature region. These results suggest that the carriers which play a crucial role in conduction are not band electrons but hopping electrons in the defect states, because the latter localized states seem to be insensitive to the pressure.

To clarify the nature of the defect states, ESR spectra of the polycrystalline samples for which $x = 0$, 0.04 and 0.08 were measured at X-band frequency (*ca.* 9.15 GHz); at temperatures below 100 K, the ESR signal was detected for each sample. Fig. 3 shows the temperature dependence of their signal intensities, which have Curie-like behaviour. This behaviour has also been observed in the magnetic susceptibility for sample with $x = 0$ below 30 K, from which a concentration of about 2% for the $S = \frac{1}{2}$ impurity has been estimated.[4] These results suggest that the observed spins arise from undimerized and hence paramagnetic $[Pt(mnt)_2]^-$ anions located near the defects in the $[Pt(mnt)_2]^-$ conducting stacks and that the spin-spin exchange interactions between these spins are weak. Fig. 4 also shows that the signal intensity for $x = 0.08$ is about three times larger than the other two, which seems to be related to the fact that this sample exhibits the lowest conductivity of the three. On the other hand, the intensity of the sample for which $x = 0.04$ is almost equal to that for $x = 0$.

The ESR spectra of these three samples at 17 K are shown in Fig. 4. All are anisotropic, which is associated with the *d*-electron character of the spins. Therefore, to evaluate the *g*-values for these three samples we have attempted to simulate the observed spectra. Calculated spectra obtained by assuming that there is only one spin system and that the line shape is Gaussian* are also shown in Fig. 4. Their spin-Hamiltonian parameters are listed in Table 2. For the pure platinum compound ($x = 0$) [Fig. 4(*a*)], the spectrum is resolved into a rhombic symmetric pattern like that found for the magnetically dilute $[Pt(mnt)_2]^-$, whose principal g values are $g_1 = 2.245$, $g_2 = 2.065$ and $g_3 = 1.827$.[5] However, our result shows a different pattern of ^{195}Pt hyperfine splittings compared with that for the magnetically dilute $[Pt(mnt)_2]^-$ (*i.e.* $A_2 > A_3 \gg A_1$), which suggests that the environment of $[Pt(mnt)_2]^-$ in $K[Pt(mnt)_2]\cdot H_2O$ is different from that of the isolated $[Pt(mnt)_2]^-$. Moreover, our result also disagrees with that obtained by Jones *et al.*[6]; they showed that $g_1 = 2.233$, $g_2 = 2.057$ and $g_3 = 1.800$ at 297.5 K, but the detailed results have not been reported yet. In contrast with the pure platinum compound, the spectra of the $[Au(mnt)_2]^-$-doped compounds [Fig. 4(*b*) and (*c*)] showed only partial resolution of the g anisotropy. The most important fact is that the sample for which $x = 0.04$ [Fig. 4(*b*)] shows a nearly axially symmetric pattern with a pronounced reduction of g anisotropy, reflecting the lower d character of the observed spins for $x = 0.04$ and hence larger ligand π character, than the other two. This indicates that the spins are more delocalized over the whole anion and perhaps along the stack. The above ESR results are consistent at least qualitatively with the conductivity results.

General.—In order to clarify our attempt at 'modification' of the central metal in a bis(mnt) metal complex salt system, we will first compare our case with similar studies of organic solid solutions cited in the Introduction. Especially, the $(mphenz)_{1-x}(phenz)_x(tcnq)$ series studied by Miller and Epstein[2] is very similar to our case in that $mphenz^{2/3+}tcnq^{2/3-}$ and $phenz^0tcnq^0$ correspond to $Pt^{II}(d^8)[(mnt)_2]^{3-}$ and $Au^{III}(d^8)[(mnt)_2]^{4-}$, respectively,† and that the solid solution is a 'mixture' of complexes of different redox potentials. They found that enhanced conductivity is observed for $x = 0.54$ due to the presence of large number of solitons.[7] However, there is one important difference between our case and the organic solid solutions. In the latter the tcnq anion stack is a main conducting stack and the defect or disorder within the cation stack caused by replacement of a cation has little influence on the electronic properties of the tcnq anion stack. Therefore, the organic solid solution having a relatively large value of x still remains highly conductive. On the other hand, in our case, partial replacement of $[Au(mnt)_2]^-$ for $[Pt(mnt)_2]^-$ may directly introduce defects into the conducting stack, although the similarity in size and shape between these two anions is better than that between the two donor molecules (*e.g.* mphenz and phenz) in the organic solid solution. Thus, one considered effect of slight replacement of the anion is to decrease the ease of hopping of the carriers. Support for this interpretation is provided by the observation that the conductivity of $K[Pt_{1-x}Au_x(mnt)_2]\cdot H_2O$ is drastically reduced at dilute concentrations of $[Au(mnt)_2]^-$, *e.g.* $x = 0.08$. This interpretation is also consistent with the fact that the ESR signal intensity for $x = 0.08$ is about three times larger than the other two.

Secondly, we will consider the excess of conductivity observed for the sample having $x = 0.04$. This is striking because the powder conductivities at room temperature are *ca.* 10^{-4} S cm^{-1} for $K[Pt(mnt)_2]\cdot H_2O$[3] but *ca.* 10^{-9} S cm^{-1} for $K[Au(mnt)_2]\cdot H_2O$.[8] Fig. 1 shows that the E_a in the low-temperature region for the samples with $x = 0$ and $x = 0.04$ is almost the same (*ca.* 0.1 eV). Moreover, their optical band gaps (*ca.* 0.9 eV for both $x = 0$ and 0.04) are not equal to those

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* This does not necessarily mean that the observed line shape is Gaussian because the fitting by using a Lorentzian line shape is good in its own way.

† The ligand molecular orbital (MO) associated with the HOMO of $Pt^{II}[(mnt)_2]^{3-}$ is half filled while the corresponding ligand MO of $Au^{III}[(mnt)_2]^{4-}$ is fully occupied. In this description we have neglected the important feature of the metal–ligand admixture in the present system for simplicity and assumed that the lone-pair electron of $[Pt(mnt)_2]^-$ resides on the ligand.

obtained from the conductivity ($E_g = 2E_a = ca.$ 0.2 eV). These indicate that the band structures of both compounds are similar and that the intrinsic semiconductor model is inappropriate for the explanation of the origin of the excess of conductivity for $x = 0.04$; the presence of defect states inside the optical gaps for both compounds is expected, as is indicated from the ESR results. Besides, the interruption of the $[Pt(mnt)_2]^-$ stack by $[Au(mnt)_2]^-$ mentioned above seems to have little effect on the conductivity for $x = 0.04$. This seems to reflect the conduction pathway based on the ligand π–π overlaps; the replacement of $[Au(mnt)_2]^-$ for $[Pt(mnt)_2]^-$ does not perfectly hinder the electron hopping from $[Pt(mnt)_2]^-$ to $[Au(mnt)_2]^-$ and *vice versa*. There seems to be another effect caused by partial replacement of the anion for $x = 0.04$.

A tentative explanation of the excess of conductivity for $x = 0.04$ is as follows. When $[Au(mnt)_2]^-$ is introduced into the dimerized stack of $[Pt(mnt)_2]^-$ the interruption of the $[Pt(mnt)_2]^-$ stack possibly causes the occurrence of undimerized $[Pt(mnt)_2]^-$ anions with one unpaired electron at the ends of the $[Pt(mnt)_2]^-$ stacks, which can provide mobile carriers. By mobile carriers we mean, here, the carriers free from the on-site Coulomb repulsion and antiferromagnetic interactions which restrict the hopping of unpaired electrons of the $[Pt(mnt)_2]^-$ along the stacks. Although these mobile carriers attributed to the disarrangement of the dimerized $[Pt(mnt)_2]^-$ stacks are more or less present in the sample having $x = 0$ and may contribute to its conductivy, the partial replacement of $[Au(mnt)_2]^-$ for $[Pt(mnt)_2]^-$ probably facilitates the creation of mobile electrons in this process. From the magnetic susceptibility of $K[Pt(mnt)_2]\cdot H_2O$, the density of the paramagnetic spins has been estimated at *ca.* 10^{-19} cm^{-3}, which is comparable to that of P-doped Si situated around the boundary concentration of the metal–non-metal transition.[9] Of course, the first effect that disturbs the hopping of the carriers might be also present in the sample having $x = 0.04$. Therefore, of these two opposing effects, the second seems to be dominant in the conductivity for $x = 0.04$.* This explanation is qualitatively consistent with the ESR results (*see above*).

In conclusion, the partial replacement of $[Au(mnt)_2]^-$ for $[Pt(mnt)_2]^-$ in $K[Pt(mnt)_2]\cdot H_2O$ probably has two opposing effects on its conductivity: (*i*) introduction of a defect into the conducting stack which disturbs the hopping of the carriers and reduces its conductivity; (*ii*) disarrangement of the dimerized stack structure which creates mobile carriers and increases the conductivity. The excess of conductivity of the sample having $x = 0.04$ seems to be attributed to the latter effect while the former effect is dominant for $x = 0.08$.

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References

1 P. M. Chaikin, J. F. Kwak, R. L. Green, S. Etemad and E. M. Engler, *Solid State Commun.*, 1976, **19**, 1201.
2 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 287.
3 S. Kutsumizu, N. Kojima, T. Ban and I. Tsujikawa, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2547.
4 S. Kutsumizu, N. Kojima, N. Watanabe and T. Ban, *J. Chem. Soc., Dalton Trans.*, 1990, 2287.
5 R. Kirmse, W. Dietzsch and B. V. Solevév, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1157.
6 M. T. Jones, J. M. Patane, P. I. Clemenson and A. E. Underhill, in *Organic and Inorganic Low-Dimensional Crystalline Materials*, eds. P. Delhaes and M. Drillon, Plenum, New York, 1987, p. 357.
7 A. J. Epstein, J. W. Kaufer, H. Rommelmann, I. A. Howard, E. M. Conwell, J. S. Miller, J. P. Pouget and R. Comès, *Phys. Rev. Lett.*, 1982, **49**, 1037.
8 S. Kutsumizu, unpublished work.
9 P. P. Edwards, *Physics and Chemistry of Electrons and Ions in Condensed Matter*, eds. J. V. Acrivos, K. Mott and A. D. Yoffe, Reidel, Dordrecht, 1984, p. 297.

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* Note that the concentration of $[Au(mnt)_2]^-$ in the sample having $x = 0.04$ is comparable to the defect concentration within the $[Pt(mnt)_2]^-$ stack for $x = 0$.