SYSTEMES INORGANIQUES CONDUCTEURS
LES ORGANOMETALLIQUES

introduct° : page 1 et 2

empilemt de Vetna cyano platinate : recouvremts

composé 1D ds chaine métallique obtenus à partir de mat par l'empt de molécules individuelles.

La formatn de liaison métal-métal subtt importantes fournit le recouvremt orbitalaire nécessaire pour l'obtent d'1 bande d'E électronique.

Des complexes métalliques dont les ligands ne sont pas trop encombrants permettent de tels contacts. Les e⁻ situés ds des orbitales de gde extension dans l'axe est ⊥ plan moyen du complexe (d_{z^2}, p_z) ↗ l'interact° le long de la chaine → caractère quasi 1D.

Le degré de recouvremt de ces orbitales détermine la formatn d'1 ~~bande d'E d'e⁻ délocalisés~~.

De + la présence d'1 nb impair d'e⁻ / ⊔ dans l'atto est nécessaire pour la formatn d'1 bande à caractère métallique.

L'extension des orbitales d_{z^2} ↘ de 5d > 4d > 3d

→ les complexes les + conducteurs seront ceux comportant des métaux de transit° de la 3e série : Pt^{2+} Ir^{2+} de transit°
≡ 6e période du tableau.

Alors que Au^{3+} n'en forme pas.

La plupart des complexes sont plan carrés (ceux intéressants ici). page 6.

Les métaux formant ces complexes plan. — sont : Co(I) Ni(II) Cu(III)
Rh(I) Ir(I) Pt(II) Pd(II)

2 critères doivent être satisfaits pour qu'1 Org Met présente 1 σ ↗ :

- bon pt régulier du complexe pour que les at de met soient alignés avec 1 courte distance $< \Sigma$ rvdw.

par ex : sel de Krogmann

$K_2[Pt(CN)_4], 3H_2O$ SC : $\sigma = 3.10^{-7}$ S cm^{-1}

$d_{Pt-Pt} = 3,5$ Å

sel de valence mixte : $K[Pt(CN)_4]\ Cl_{0,32}(H_2O)_3$

$\sigma = 2.10^{2}$ S cm^{-1}

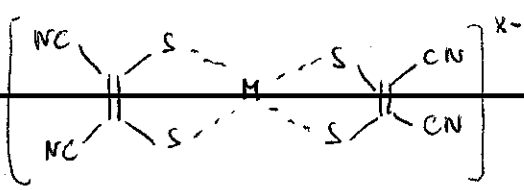
$d_{Pt-Pt} = 2,88$ Å

- bande de conduct partiellant occupée : page 3

→ chaine pouvant former 1 BC.

Ceci implique qu'il y ait 1 oxydat, enlevant des e⁻ de dz^2

Pour 1 métal, subir 1 oxydat partielle nécessite 2 états stables d'oxydat.



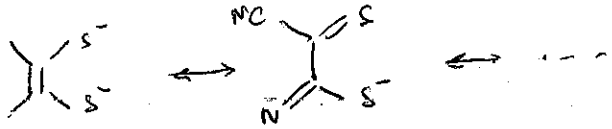
: page 5 avec Pt : état SC

bis(maléonitrile dithiolate)

mnt

Voir complexes page 5 : tous SC

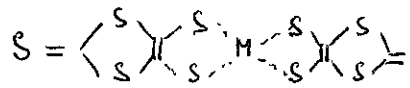
intérêt de ces ligands : capable de stabiliser des états inaccessibles d'oxydat, car il sont capables d'accepter 1 excès d'e⁻ en réduisant (sur S) en réduisant les répulsions de Coulomb en distribuant la charge sur les doubles liaisons :



→ conduct° quasi 1D : page 7 : séparé par les molécules d'H₂O.
→ ≈ 100 S cm⁻¹
empilements éclipsés le long de $\vec{c}$
et feuillets sur $\vec{a}$ $\vec{b}$

dans les chaines : S_S courtes ($< \Sigma r_{dw}$)
dans les feuillets : courtes =ᵗ.
(entre les chaine)
recouvrement intra empilement prépondérant → 1D (selon $\vec{c}$)
délocalisat° des e⁻ : orbitales d du platine (page 6).

Autre type de ligands :



bis (dimercaptoisotrithione) M ≡ $(dmit)_2^{x-}$ M M : Ni, Pt, Pd

syst conducteurs : molécules planes, e⁻ π délocalisés, tendance à s'empiler.
→ formaᵗ d'1 BC partiellement remplie par oxydaᵗ partielle.

$$\left[N_i\left[dmit\right]_2\right]^- \overset{\oplus}{N}Bu^t_4 \xrightarrow{-e^-} \left[N_i(dmit)_2\right](N Bu^t_4)_{0,29}$$

~~→ page 7 en bas : empilemᵗ.~~

page 8 : empilemᵗ des complexes : 4 décalage 4
page 9 : recouvremᵗ des (dmit)Ni à l'intérieur et entre
2 tétrades : à l'intérieur : a, b
entre : c

On peut aussi : $TTF\left[N_i(dmit)_2\right]_2$ → supra ⊓ à TbT : page 11
métallique.

page 12 : empilemᵗ de Ni régulier
représentaᵗ des distances de la structure
→ empᵗ uniforme ségrégué de TTF
——— de Ni(dmit)) interaᶜᵗ courtes S_S entre empilemᵗ

Ces contacts évitent la transition de Peierls.

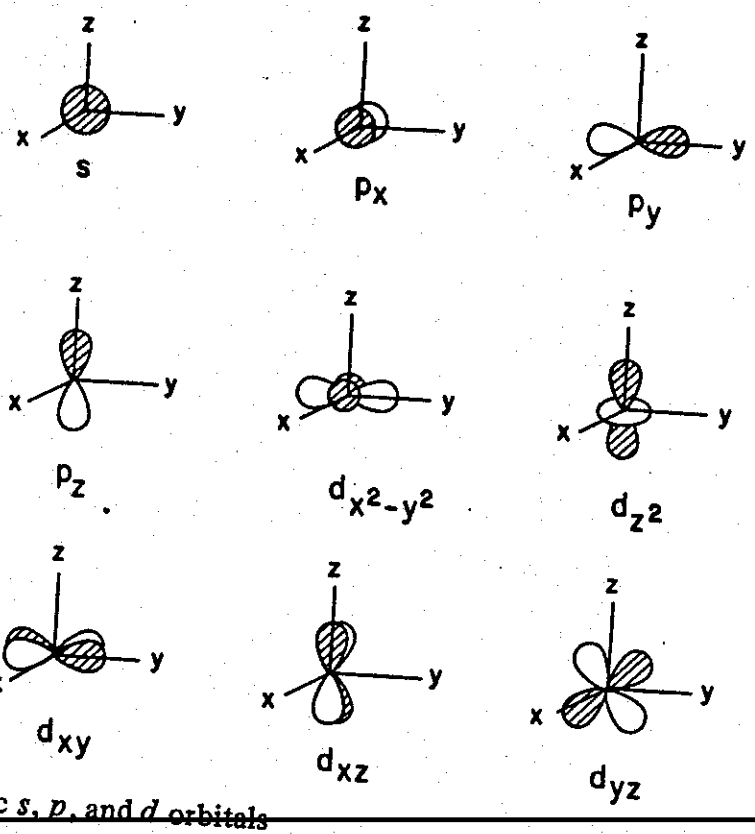
$\sigma = 300$ S cm^{-1} 300 K

$\sigma \geq 10^5$ S cm^{-1} 4 K

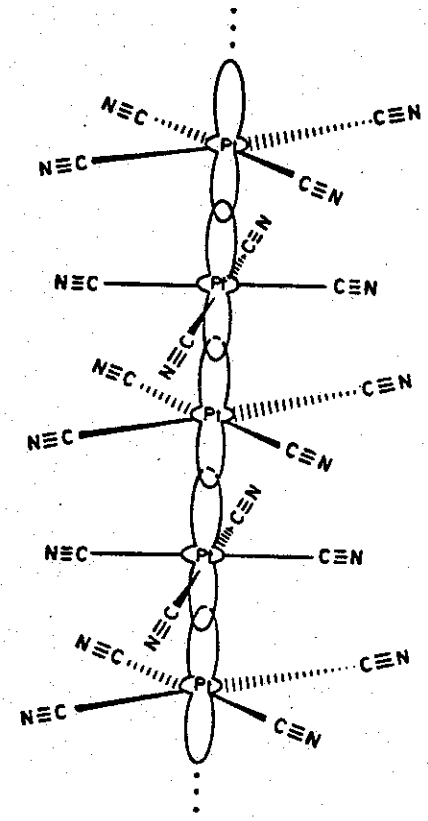
supra sous 7 kbar $T_c = 1{,}62$ K

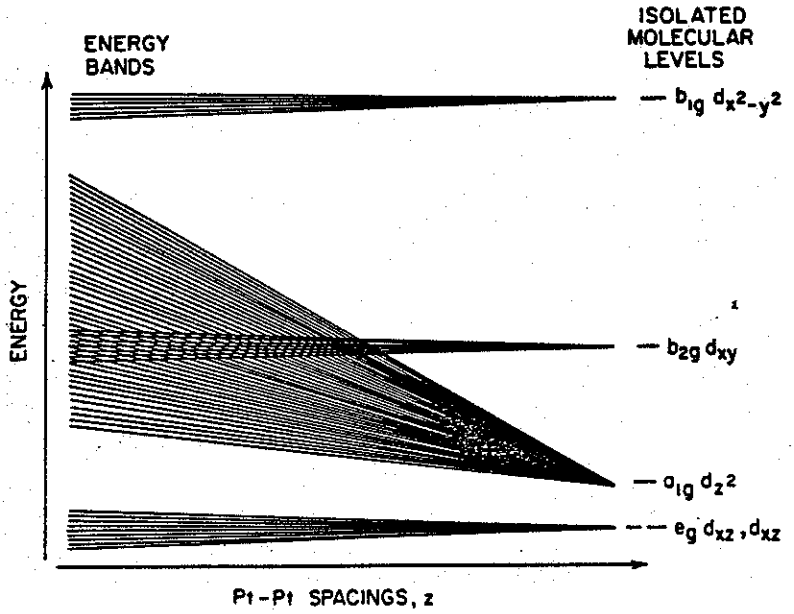
et aussi : $\left[Ni(dmit)_2\right]_2^-(CH_3)_4N$: $T_c = 5$ K sous 4 kbar

LES ORGANOMETALLIQUES

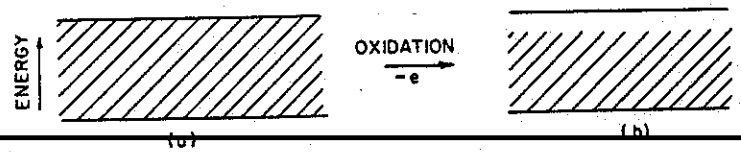


Atomic *s*, *p*, and *d* orbitals


N≡C
C≡N
Pt



Schematic correlation diagram for the electronic energy levels of isolated $Pt(CN)_4^{2-}$ as the ions approach each other.



Schematic illustration of oxidation of a filled d_{z^2} energy band; (a) forming a partially occupied d_{z^2} electron energy band, (b) assuming a constant bandwidth before and after partial oxidation. Note that the change in metal–metal spacing will affect the bandwidth.

Crystal Structure and Conductivities for Several Krogmann-Type Conductors[a]

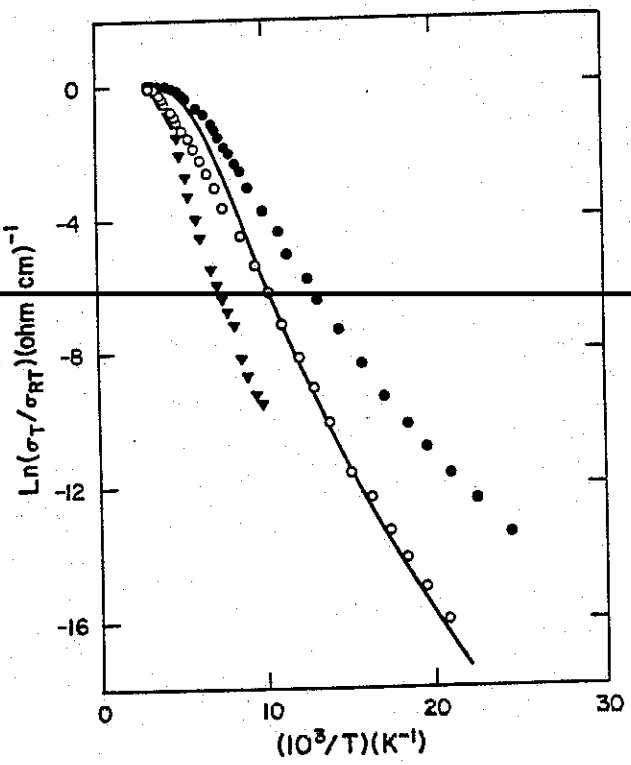
Conductor	Space group[b]	d_{Pt-Pt} (Å) at 298 K	Conductivity[c] $(ohm\ cm)^{-1}$	Color
Pt metal		2.775	9.4×10^4	Metallic
$K_2[Pt(CN)_4]Br_{0.30} \cdot 3H_2O$	*P4mm*	2.89	4–1050	Bronze
$K_2[Pt(CN)_4]Cl_{0.30} \cdot 3H_2O$	*P4mm*	2.87	~200	Bronze
$K_2[Pt(CN)_4]Br_{0.15}Cl_{0.15} \cdot 3H_2O$	*P4mm*			
$Rb_2[Pt(CN)_4]Cl_{0.30} \cdot 3H_2O$	*P4mm*	2.877, 2.924	10	Bronze
$Cs_2[Pt(CN)_4]Cl_{0.30}$	*I4/mcm*	2.859	~200	Bronze
$(NH_4)_2(H_3O)_{0.17}[Pt(CN)_4]Cl_{0.42} \cdot 2.83H_2O$	*P4mm*	2.910, 2.930	0.4	Bronze
$Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5H_2O$	*P4b2*	2.877		Reddish copper
$Rb_3(H_3O)_{0.x}[Pt(CN)_4](O_3SO \cdot H \cdot OSO_3)_{0.49} \cdot (1\text{-}x)H_2O$	$P\bar{1}$	2.826		Copper
$K_{1.75}[Pt(CN)_4] \cdot 1.5H_2O$	$P\bar{1}$	2.965, 2.961	115–125	Bronze
$Rb_{1.75}[Pt(CN)_4] \cdot 1.5H_2O$	*d*	2.94	1	Bronze
$Cs_{1.75}[Pt(CN)_4] \cdot 1.5H_2O$	*d*	2.88	~25	Bronze
$K_2[Pt(CN)_4](FHF)_{0.30} \cdot 3H_2O$	*P4mm*	2.918, 2.928		Reddish bronze
$Rb_2[Pt(CN)_4](FHF)_{0.40}$	*I4/mcm*	2.798	2300	Gold
$Rb_2[Pt(CN)_4](FHF)_{0.26} \cdot 1.7H_2O$	*C2/c*	2.89		Greenish bronze
$Cs_2[Pt(CN)_4](FHF)_{0.39}$	*I4/mcm*	2.833	1600	Reddish gold
$Cs_2[Pt(CN)_4](FHF)_{0.23}$	*I4/mcm*	2.872	250–350	Reddish bronze
$Cs_2[Pt(CN)_4]F_{0.19}$	*Immm*	2.886		Reddish gold
$[C(NH_2)_3]_2Pt(CN)_4](FHF)_{0.26} \cdot xH_2O$		2.90		Bronze
$[C(NH_2)_3[Pt(CN)_4]Br_{0.25} \cdot H_2O$	*I4cm*	2.908		Bronze

[a]Data taken in part from Williams and Schultz (1979a).

[b]For the space group *P4mm* the Pt–Pt intrachain distances are not required to be equal, but often appear to be so. When they have been determined to be different both distances are tabulated.

[c]Results are for a range of literature values for room temperature and by the four point probe dc conductivity method.

[d]The crystal class is monoclinic but the space group is unknown. The lattice constants for the Cs salt are $a = 18.35$, $b = 5.760$, $c = 19.91$ Å, and $\beta = 109.03°$; for the Rb salt the lattice constants are $a = 10.56$, $b = 33.2$, $c = 11.74$ Å, and $\beta = 114.23°$.



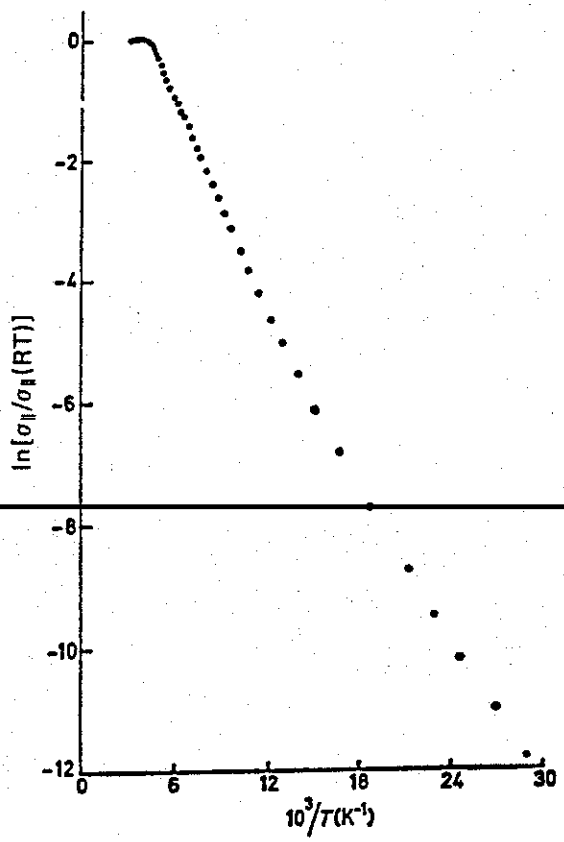
Temperature dependence of the in-chain dc conductivity for the four isostructural type *P* compounds (space group *P4mm*): full line, KCP(Br); open circles, RbCP(Cl); closed circles, KCP(Cl); and triangles, ACP(Cl). [From Williams *et al.* (1982).]

Electrical Conductivities of Several Dithiolate Salts

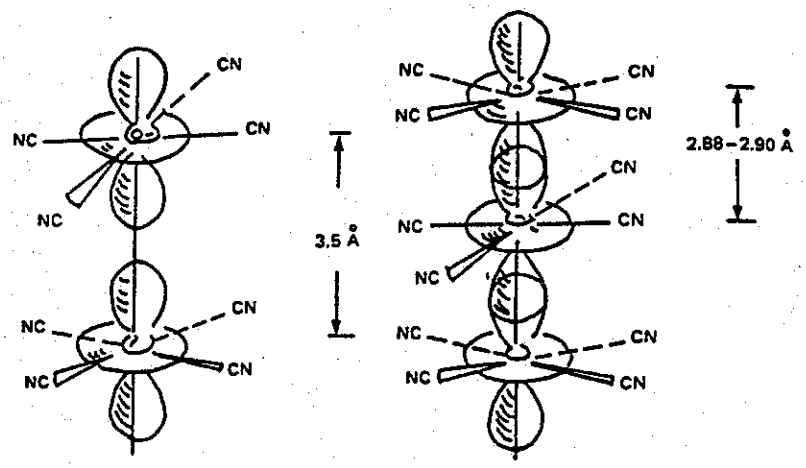
Cation	Anion	σ_{RT} (Compressed pellet)[a] (ohm cm)$^{-1}$
NEt_4^+	$[Ni(S_2C_4N_2)_2]^-$	1.0×10^{-8}
NH_4^+[b] (a)	$[Ni(S_2C_4N_2)_2]^-$	4.0×10^{-4}
(b)		1.0
$^1Na^+$[b] (a)	$Ni(S_2C_4N_2)_2]^-$	4.0×10^{-4}
(b)		2.5×10^{-1}
NEt_4^+	$[Pd(S_2C_4N_2)_2]^-$	2.5×10^{-8}
NH_4^+	$[Pd(S_2C_4N_2)_2]^-$	1.1
Na^+	$[Pd(S_2C_4N_2)_2]^-$	4.0×10^{-1}

[a] Taken in part from Perez-Albuerne *et al.* (1977).

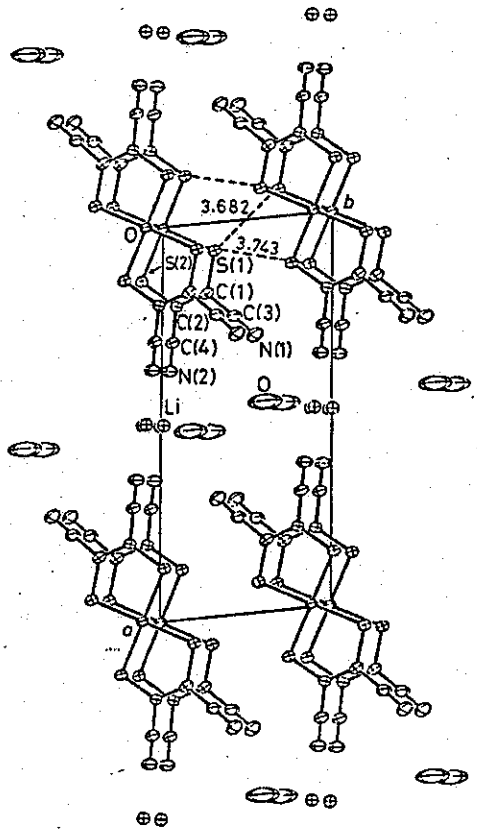
[b] The differences for the NH_4^+ salt a and b for Na were attributed to the state of hydration (a being anhydrous while b is hydrated). It was also determined that two forms of salts could be crystallized, which had different conductivities.



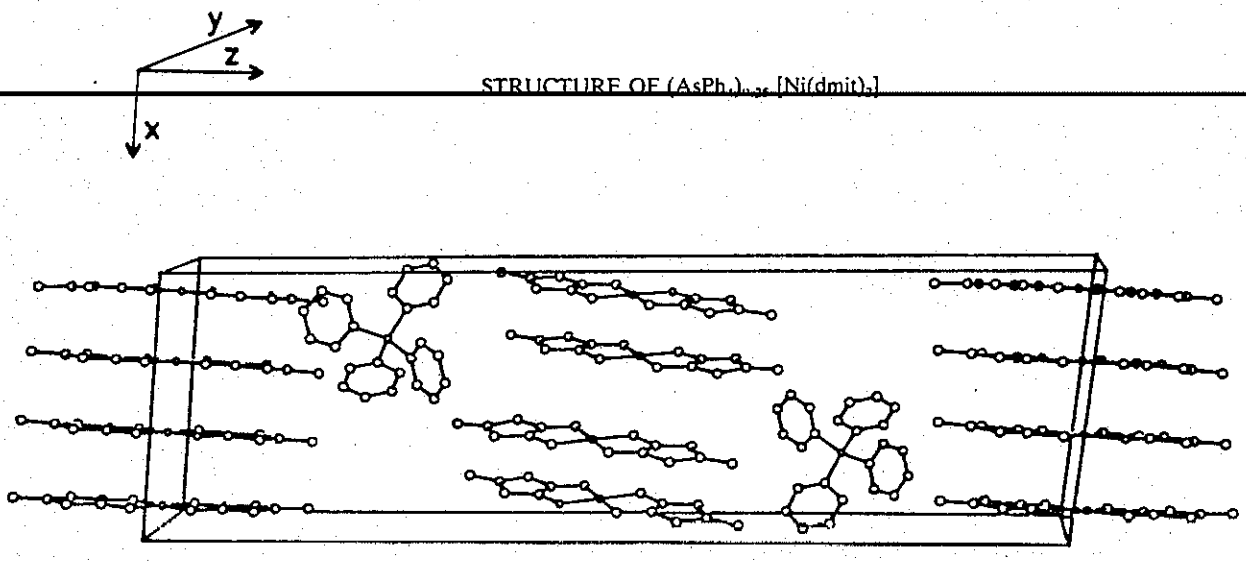
Variation of conductivity with temperature $\ln[\sigma_l/\sigma_l(RT)]$ for a single crystal of $Li_x[Pt(S_2C_4N_2)_2] \cdot 2H_2O$. [From Underhill and Ahmad (1981).]



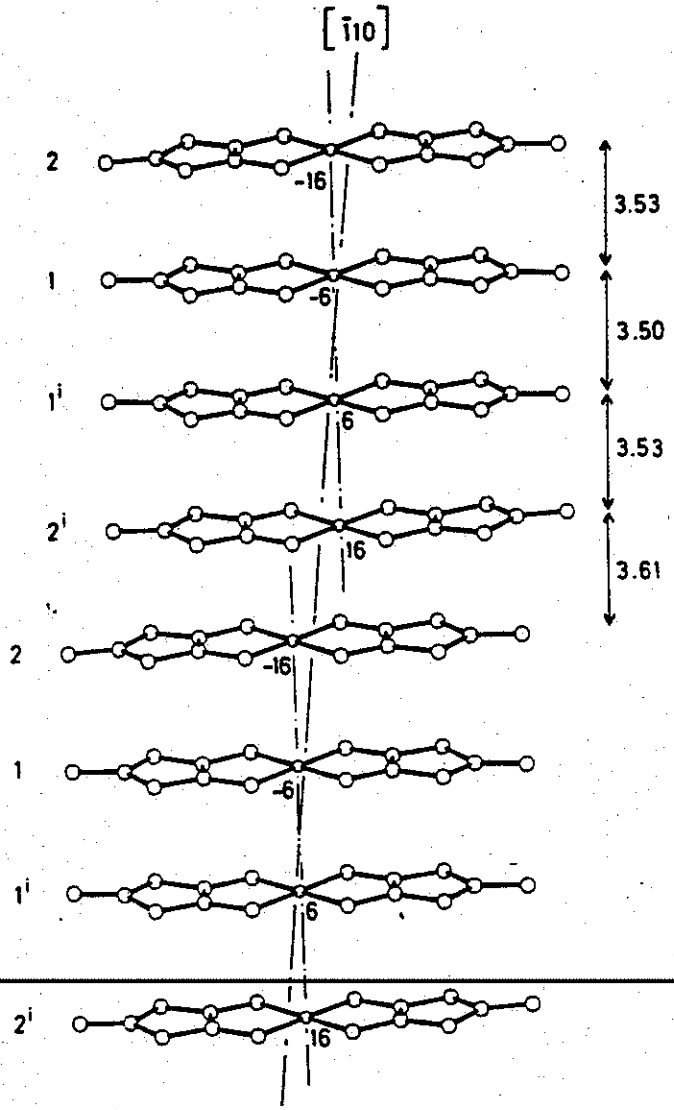
Comparison of chains of square planar $Pt(CN)_4^{x-}$ groups in (a) $K_2[Pt(CN)_4]$ with $\sigma = 5.0 \times 10^{-7}$ (ohm cm)$^{-1}$ and (b) $K_2[Pt(CN)_4]\ Br_{0.3} \cdot 3H_2O$ with $\sigma = 4.83$ (ohm cm)$^{-1}$ (298 K).



The c^* axis projection of the crystal structure of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$.



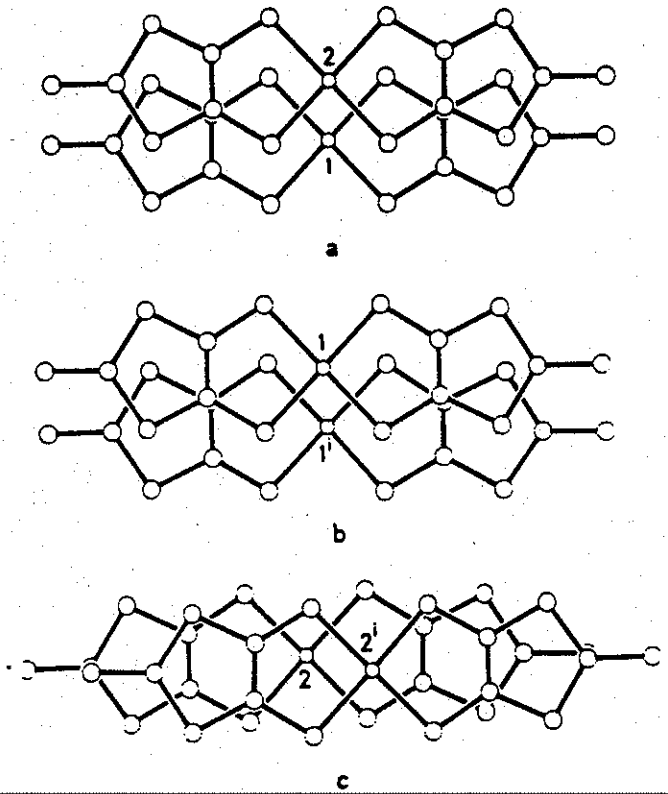
Perspective view of the molecular packing.



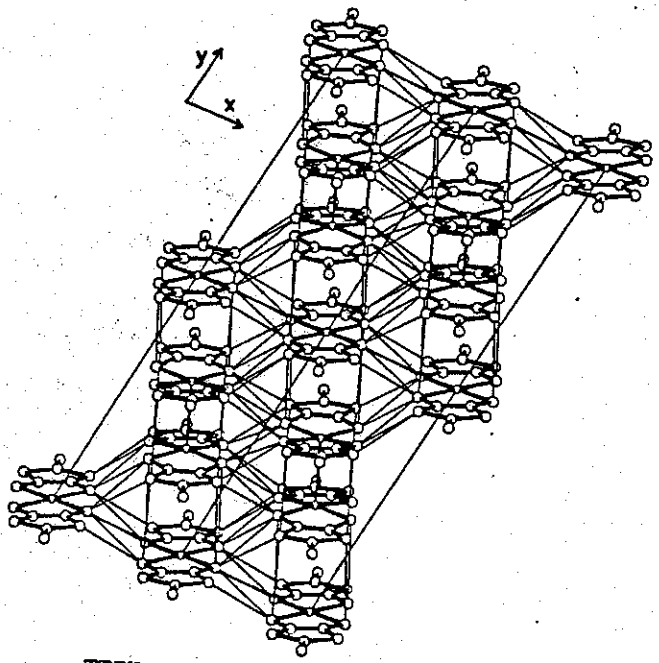
Orthogonal projection of a stack onto a plane defined by the stacking direction [1̄10] and the molecular axis S(51)—S(101). The level of the Ni atoms above this plane is indicated in arbitrary units. Interplanar distances in Å. Number 1 and 2 refer to Ni(1) and Ni(2) respectively and superscript i indicates symmetry through a centre of inversion.

structure of $(AsPh_4)_{0,25}[Ni(dmit)_2]$

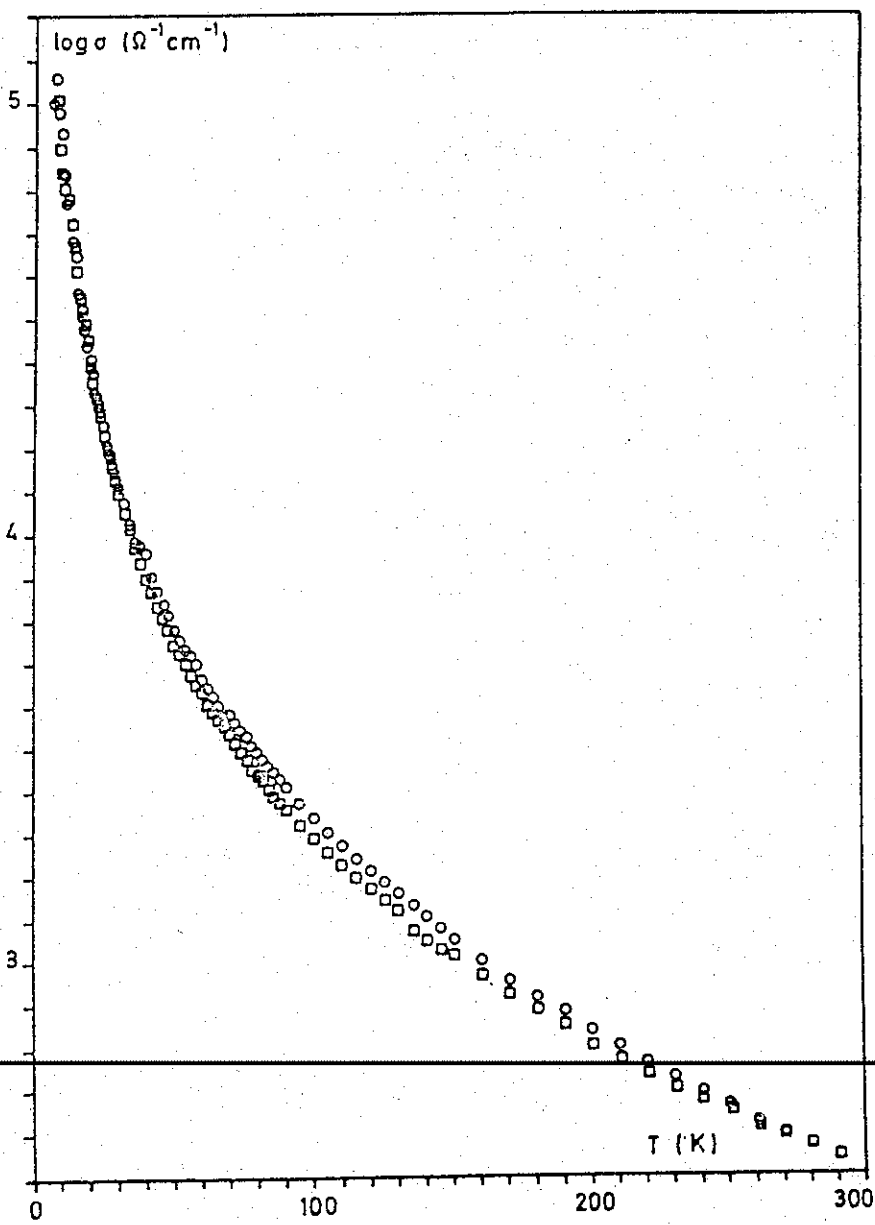
STRUCTURE OF $(AsPh_4)_{0.25}$ $[Ni(dmit)_2]$



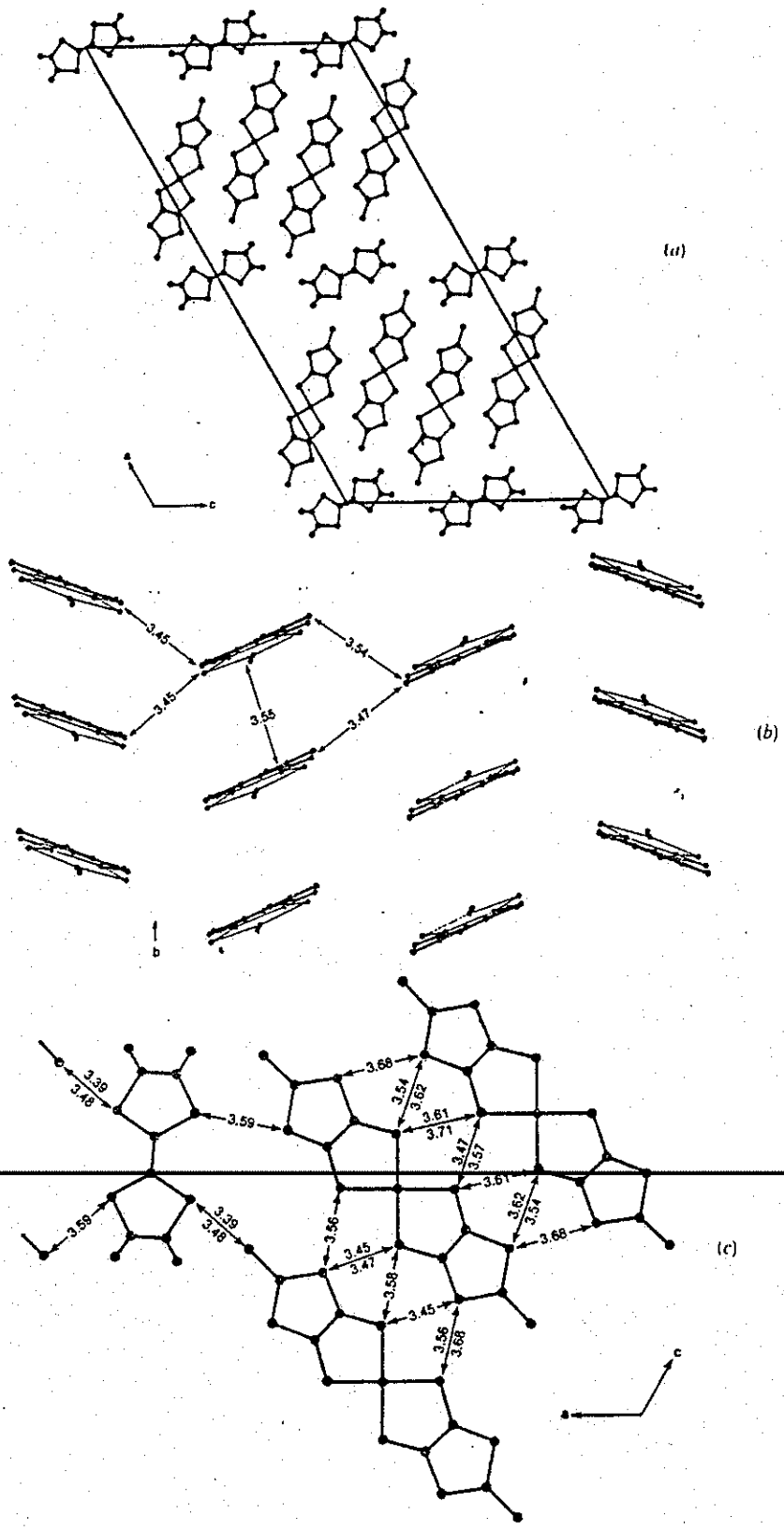
Overlap of $Ni(dmit)_2$ entities within a tetrad (*a*, *b*) and between two tetrads (*c*). Number 1 and 2 refer to Ni(1) and Ni(2), respectively, and superscript i indicates symmetry through a centre of inversion.



.. $TTF[Pt(dmit)_2]_3$. Parallel view of a layer containing stacks of $Pt(dmit)_2$ units. Within a stack, monomers and dimers alternate along $[1\bar{1}0]$. For the sake of clarity, the (001) plane is tilted out of the projection plane by 18° around an axis perpendicular to $[1\bar{1}0]$. Thin lines indicate S···S distances shorter than 3.70 Å.



— Variation de la conductivité en fonction de la température du composé TTF[Ni (dmit)$_2$]$_2$ (référence [29]); (○ = températures décroissantes; □ = températures croissantes).



structure de $TTF[Ni(dmit)_2]_2$