PREPARATION AND PROPERTIES OF Ni(IV), Pd(IV) AND Pt(IV) TRISDITHIOCARBAMATO COMPLEXES

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Oxidation of *N,N*-dialkyldithiocarbamato (R_2dtc) complexes of Ni(II), Pd(II) and Pt(II) with 3,5-bis(*N,N*-dialkyliminium)-1,2,4-trithiolane ion $(R_4bitt)^{2+}$ containing compounds and with $M(R_2dtc)X_2$ ($M = Cu, Au$; $X = Cl, Br$) is reported. From the oxidation of $Ni(R_2dtc)_2$ the compounds $Ni(R_2dtc)_3X$ ($X = Cl, Br, FeCl_4$) were obtained. The oxidation of $Pd(R_2dtc)_2$ with $R_4bitt^{2+}Cu_2X_6^{2-}$ ($X = Cl, Br$) resulted in the new compounds $[Pd(R_2dtc)_3]_2-Cu_2X_6$.

The new compound $Pt(R_2dtc)_3CuBr_2$ could be obtained by the oxidation of $Pt(R_2dtc)_2$ with either $(R_4bitt)^{2+}Cu_2Br_6^{2-}$ or $Cu(R_2dtc)Br_2$, or by the reaction of $Pt(R_2dtc)_3Br$ with $CuBr_2$. The analogous copper chloride compound was prepared from $(R_4bitt)^{2+}Cu_2Cl_6^{2-}$ with $Pt(R_2dtc)_2$. The compound $Pt(R_2dtc)_3AuBr_2$ was prepared from $Pt(R_2dtc)_2$ and $Au(R_2dtc)Br_2$. The metal-sulfur infrared stretching frequencies are in accord with the assumption that in all these compounds the metal atoms Ni(IV), Pd(IV) and Pt(IV) have a D_3 symmetry. Conductivity measurements showed the platinum complexes to be 1:1 electrolytes.

Introduction

The excessive halogenation of some dithiocarbamato complexes *e.g.* $Fe(R_2dtc)_3$ and $[Cu(R_2dtc)]_4$ was earlier supposed to yield $[(R_2dtc)_2]^{2+}[FeX_4]_2$ and $[(R_2dtc)_2]^{2+}[Cu_2X_6]^{2+}$. The structure of the $[(R_2dtc)_2]^{2+}$ ion was postulated by *Willemse* and *Steggerda*². Further investigations, however, indicated the ion to be composed of a trithiolane ring. The most convincing information was obtained by an X-ray analysis of the compound, which was assumed to be $[(et_2dtc)_2]^{2+}$

¹ P. T. Beurskens, J. A. Cras, Th. W. Hummelink and J. G. M. van der Linden, *Rec. Trav. Chim.* **89**, 984 (1970).

² J. Willemse and J. J. Steggerda, *Chem. Comm.* 1123 (1969).

$[\text{Hg}_2\text{I}_6]^{2-}$. This analysis revealed the compound has to be formulated as³:

i.e., 3,5-bis(*N,N*-diethyliminium)-1,2,4-trithiolane-di- μ -iodotetraiododimercurate (II).

For the 3,5-bis(*N,N*-dialkyliminium)-1,2,4-trithiolane ion we shall use the notation $[\text{R}_4\text{bitt}]^{2+}$.

In a previous communication¹ we reported the synthesis of the compound $[\text{Au}(\text{bu}_2\text{dtc})_2]^+[\text{CuBr}_2]^-$ by the following reactions:

As we are interested in the oxidizing properties of compounds, containing the $[\text{R}_4\text{bitt}]^{2+}$ ion, we carried out some reactions of these compounds with the dithiocarbamate complexes of nickel, palladium and platinum and with the zinc, cadmium and mercury dithiocarbamates.

The results of the reactions with the former three compounds are reported in this communication, whereas those results with the latter three compounds will be dealt with in a forthcoming publication.

Experimental section⁴

The starting materials were obtained as described in the literature: $\text{Ni}(\text{et}_2\text{dtc})_2$ from $\text{Na}(\text{et}_2\text{dtc}) \cdot 3\text{H}_2\text{O}$ (Baker) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck); $\text{Ni}(\text{bu}_2\text{dtc})_2$, $\text{Pd}(\text{bu}_2\text{dtc})_2$ and $\text{Pt}(\text{bu}_2\text{dtc})_2$ following the general procedure for the synthesis of dithiocarbamates⁵

³ P. T. Beurskens, W. P. J. H. Bosman and J. A. Cras, *J. Cryst. Mol. Struct.* **2**, (1972).

⁴ We gratefully acknowledge the assistance of Mr. W. F. J. H. Sieben in the preparative work.

⁵ G. D. Thorn and R. A. Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam (1962).

from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, K_2PdCl_4 (Drijfhout) and K_2PtCl_4 (Drijfhout), respectively. The preparation of the following compounds is described in the given references: $[\text{et}_4\text{bitt}]^{2+}[\text{FeCl}_4^-]_2$, $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{Cl}_6]^{2-}$, $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{Br}_6]^{2-}$, $\text{Cu}(\text{bu}_2\text{dtc})\text{Br}_2$, $\text{Au}(\text{bu}_2\text{dtc})\text{Br}_2$ ⁸ and $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+\text{Br}^-$ ⁹.

Analyses. Heavy metals were analysed by atomic absorption photometric methods, using dilute *aqua regia* solutions as standards. The other elemental analyses were carried out in the micro-analytical department of this university.

Preparations

I. Reactions of $[\text{R}_4\text{bitt}]^{2+}$ containing compounds with the dithiocarbamate complexes of nickel, palladium and platinum

a) Reaction of $\text{Ni}(\text{et}_2\text{dtc})_2$ with $[\text{et}_4\text{bitt}]^{2+}[\text{FeCl}_4^-]_2$

To a solution of one mole of $\text{Ni}(\text{et}_2\text{dtc})_2$ in chloroform, a suspension of half a mole of $[\text{et}_4\text{bitt}]^{2+}[\text{FeCl}_4^-]_2$ in chloroform was added. A clear solution was obtained by stirring the reaction mixture for half an hour. After addition of ligroin (40–60°), a crystalline product of $[\text{Ni}(\text{et}_2\text{dtc})_3]^+[\text{FeCl}_4^-]$ was obtained.

b) Reaction of $\text{Ni}(\text{bu}_2\text{dtc})_2$ with $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{Br}_6]^{2-}$ and with $[\text{bu}_4\text{bitt}]^{2+}[\text{AuBr}_4^-]_2$

When the same procedure was used for these reaction components as described for the reaction of $\text{Ni}(\text{et}_2\text{dtc})_2$ with $[\text{et}_4\text{bitt}]^{2+}[\text{FeCl}_4^-]_2$, oily products were obtained. This complication could be avoided when the following modification was used. To the chloroform solution of the reaction mixture an equal volume of water was added and this mixture was shaken for twelve hours. After addition of ligroin (40–60°) or diethyl ether to the chloroform layer, a precipitate of $[\text{Ni}(\text{bu}_2\text{dtc})_3]^+\text{Br}^-$ was obtained in both cases. In the aqueous layers copper and gold, respectively, could be detected.

c) Oxidation of $\text{Pd}(\text{bu}_2\text{dtc})_2$ with $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$)

To solutions of one mole $\text{Pd}(\text{bu}_2\text{dtc})_2$ in chloroform, suspensions of half a mole of $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{Cl}_6]^{2-}$ and $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{Br}_6]^{2-}$

⁶ H. C. Brinkhoff, Thesis, Nijmegen (1970).

⁷ P. T. Beurskens, J. A. Cras and J. J. Steggerda, *Inorg. Chem.* 7, 810 (1968).

⁸ H. J. A. Blaauw, R. J. Nivard and G. J. M. van der Kerk, *J. Organometal. Chem.* 2, 236 (1964).

⁹ J. A. Cras and J. Willemse, to be published.

were added. Clear solutions were obtained by stirring the reaction mixtures for half an hour. After addition of diethyl ether to the solutions a red crystalline compound $\text{Pd}(\text{bu}_2\text{dtc})_3\text{CuCl}_3$ (m.p. 104–105°) and a black-brown crystalline compound $\text{Pd}(\text{bu}_2\text{dtc})_3\text{CuBr}_3$ (decomp. > 90°) was obtained in the respective mixtures. Some coprecipitated $\text{Cu}(\text{bu}_2\text{dtc})\text{Cl}_2$ and $\text{Cu}(\text{bu}_2\text{dtc})\text{Br}_2$ could be removed by washing thoroughly with diethyl ether.

Anal. Calcd. for $\text{PdC}_{27}\text{H}_{54}\text{N}_3\text{S}_6\text{CuCl}_3$: Pd, 11.96; C, 36.46; H, 6.13; N, 4.73; Cu, 7.14; Cl, 11.96.

Found: Pd, 12.05; C, 36.59; H, 6.07; N, 4.86; Cu, 7.20; Cl, 12.40.

Calcd. for $\text{PdC}_{27}\text{H}_{54}\text{N}_3\text{S}_6\text{CuBr}_3$: Pd, 10.40; C, 31.70; H, 5.33; N, 4.11; Cu, 6.21; Br, 23.44.

Found: Pd, 10.44; C, 31.13; H, 5.11; N, 4.11; Cu, 6.36; Br, 23.69.

d) *Oxidation of $\text{Pt}(\text{bu}_2\text{dtc})_2$ with $[\text{bu}_4\text{bitt}]^{2+}[\text{Cu}_2\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$)*

The same procedure as described for the oxidation of $\text{Pd}(\text{bu}_2\text{dtc})_2$ was performed with the platinum compound. Yellow crystals of $\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) were obtained with melting points 153–154° and 141.5–142.5°, respectively.

Anal. Calcd. for $\text{PtC}_{27}\text{H}_{54}\text{N}_3\text{S}_6\text{CuCl}_2$: C, 34.40; H, 5.79; N, 4.46; Cu, 6.74; Cl, 7.52.

Found: C, 33.90; H, 5.50; N, 4.53; Cu, 6.74; Cl, 7.76.

Calcd. for $\text{PtC}_{27}\text{H}_{54}\text{N}_3\text{S}_6\text{CuBr}_2$: C, 31.43; H, 5.29; N, 4.07; S, 18.65; Cu, 6.16; Br, 15.49.

Found: C, 31.36; H, 5.46; N, 4.06; S, 18.47; Cu, 6.20; Br, 15.25.

II. *Oxidation of $\text{Ni}(\text{bu}_2\text{dtc})_2$, $\text{Pd}(\text{bu}_2\text{dtc})_2$ and $\text{Pt}(\text{bu}_2\text{dtc})_2$ with $\text{Cu}(\text{bu}_2\text{dtc})\text{Br}_2$ and with $\text{Au}(\text{bu}_2\text{dtc})\text{Br}_2$*

Solutions of one mole of $\text{Ni}(\text{bu}_2\text{dtc})_2$ in chloroform were added to a solution of one mole of $\text{Cu}(\text{bu}_2\text{dtc})\text{Br}_2$ or $\text{Au}(\text{bu}_2\text{dtc})\text{Br}_2$ in chloroform. Oily substances were obtained after addition of diethyl ether to the reaction mixtures. Whereas infrared spectra of these oils indicated impure $\text{Ni}(\text{bu}_2\text{dtc})_3\text{Br}$ to be present, no attempts were made to purify the products. When the same procedures were carried out for $\text{Pd}(\text{bu}_2\text{dtc})_2$ no reactions were observed at all. $\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuBr}_2$ and

$\text{Pt}(\text{bu}_2\text{dtc})_3\text{AuBr}_2$ however could be obtained in 90% and 85% yield, respectively, using the procedure described above. The melting point of $\text{Pt}(\text{bu}_2\text{dtc})_3\text{AuBr}_2$ is 135.5–137°.

Anal. Calcd. for $\text{PtC}_{27}\text{H}_{54}\text{N}_3\text{S}_6\text{AuBr}_2$: C, 27.83; H, 4.68; N, 3.61; Au, 16.9; Br, 13.7.

Found: C, 27.45; H, 4.45; N, 3.63; Au, 17.3; Br, 13.9.

III. Reaction of $\text{Pt}(\text{bu}_2\text{dtc})_3\text{Br}$ with CuBr_2

As in the reaction of $[\text{Au}(\text{bu}_2\text{dtc})_2]^+\text{Br}^-$ with CuBr_2 , which yields $[\text{Au}(\text{bu}_2\text{dtc})_2]^+[\text{CuBr}_2]^- + \frac{1}{2}\text{Br}_2$, $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+[\text{CuBr}_2]^-$, could be obtained from solutions of $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+\text{Br}^-$ and CuBr_2 in absolute ethanol.

Physical measurements

Infrared spectra in the region of 4000–625 cm^{-1} were examined in KBr pellets with a Perkin-Elmer 257 infrared spectrophotometer. In the region 700–200 cm^{-1} the spectra were measured with an Hitachi EPI-L instrument. These spectra were recorded in Nujol mulls unless otherwise stated.

Magnetic susceptibility measurements were performed with a standard Gouy-type balance.

Conductivity. The molar conductivities were measured in nitrobenzene solutions at 25°.

Nuclear Magnetic Resonance. The NMR spectra were recorded on a Varian HA-100 instrument.

Results and discussion

The compounds $\text{Pd}(\text{bu}_2\text{dtc})_3\text{CuCl}_3$ and $\text{Pd}(\text{bu}_2\text{dtc})_3\text{CuBr}_3$ decompose in several organic solvents, therefore conductivity measurements, NMR and electronic spectra could not be taken. With the aid of UV techniques $\text{Pd}(\text{bu}_2\text{dtc})_2$ and $\text{Cu}(\text{bu}_2\text{dtc})\text{X}_2$ ($\text{X} = \text{Cl}$ and Br , respectively) could be proved to be the decomposition products in chloroform.

Magnetic susceptibility measurements indicated that in the temperature range 103–293 °K the Curie-Weiss law is followed.

For the chlorine compound a Weiss temperature of -5°K and a magnetic moment of 2.10 BM are found, the values for the bromine compound are 0°K and 2.06 BM, respectively. The results agree with the assumption that diamagnetic Pd(IV) and Cu(II) ($S = \frac{1}{2}$) are present in these compounds. In the far infrared spectra the copper halogen stretching frequencies indicated the presence of dimeric halogenocuprate ions (Table I).

In the planar ions $[\text{Cu}_2\text{X}_6]^{2-10}$ two terminal metal halogen stretching frequencies (B_{2u} and B_{3u}) and two bridging frequencies (B_{2u} and B_{3u} as well) should be present. One of the bridging frequencies in $\{[\text{Pd}(\text{bu}_2\text{dtc})_3]^+\}_2[\text{Cu}_2\text{Br}_6]^{2-}$ could not be observed as it is expected below 200 cm^{-1} . The other values are in agreement with those found for the compounds $\text{K}_2\text{Cu}_2\text{Cl}_6$ and $\text{K}_2\text{Cu}_2\text{Br}_6$, respectively¹¹.

Table I

Copper-halogen stretching frequencies in cm^{-1}

	(Cu—X _t)	(Cu—X _b)
$[\text{Pd}(\text{bu}_2\text{dtc})_3]_2\text{Cu}_2\text{Cl}_6$	310 (broad)	275 240
$\text{K}_2\text{Cu}_2\text{Cl}_6$ ¹¹	301 193	278 236
$[\text{Pd}(\text{bu}_2\text{dtc})_3]_2\text{Cu}_2\text{Br}_6$	245	223
$\text{K}_2\text{Cu}_2\text{Br}_6$ ¹¹	237 122	224
	t = terminal	b = bridged

In contrast to the palladium compounds the platinum compounds contain two halogen atoms per formula unit. It is reasonable to assume $[\text{CuCl}_2]^-$, $[\text{CuBr}_2]^-$, and $[\text{AuBr}_2]^-$ to be present in these complexes. In view of the linear structure of these ions ($D_{\infty h}$) two metal halogen modes are infrared active, Σ_u^+ and Π_u .

For $[\text{AuCl}_2]^-$ the Σ_u^+ absorption is found at 340 cm^{-112} . Considering the mass effect only, the calculated values should be 393 cm^{-1} for $[\text{CuCl}_2]^-$, 313 cm^{-1} for $[\text{CuBr}_2]^-$ and 248 cm^{-1} for $[\text{AuBr}_2]^-$.

¹⁰ P. H. Vossos, L. D. Jennings and R. E. Rundle, J. Chem. Phys. **32**, 1590 (1963).
P. H. Vossos, D. R. Fitzwater and R. E. Rundle, Acta Cryst. **16**, 1037 (1963).

R. D. Willett, C. Dwiggin, R. F. Kruh and R. E. Rundle, J. Chem. Phys. **38**, 2429 (1963).

¹¹ D. M. Adams and P. J. Lock, J. Chem. Soc. (A) 620 (1967).

¹² D. M. Adams, Metal-Ligand and Related Vibrations, E. Arnold Ltd, London (1967).

Absorption bands found at 407 cm^{-1} for $\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuCl}_2$, at 325 cm^{-1} for $\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuBr}_2$ and at 253 cm^{-1} for $\text{Pt}(\text{bu}_2\text{dtc})_3\text{AuBr}_2$ are therefore ascribed to the asymmetric metal-halogen stretching frequencies (Σ_u^+). The Π_u frequencies are expected to lie in region below 200 cm^{-1} .

The C—N and M—S stretching frequencies of the complexes are in good agreement with those found in the metal trisdithiocarbamato complexes with bromide and iodide as anions⁹. The metal-sulfur stretching frequencies in the metaltrisdithiocarbamato complexes of nickel, palladium and platinum are given in Table II. Considering only the sulfur atoms around the central metal atom, the coordination symmetry is nearly O_h , and only one normal vibration belonging to a M—S stretching frequency is expected to be found. In this way *Brinkhoff*⁶ ascribes the 387 cm^{-1} absorption band in $[\text{Ni}(\text{bu}_2\text{dtc})_3]^+$ to the Ni—S stretching frequency. When however the R_2NC chain is taken into account, the symmetry is D_3 . In that case three normal modes of vibration belonging to the M—S stretching frequency are infrared active ($A_2 + 2E$). Assuming the M—S stretching frequencies to be subject to mass changes only, we found in the trisdithiocarbamates of nickel, palladium and platinum, three absorption peaks with a remarkable agreement between the observed and calculated values when the spectrum of $[\text{Pd}(\text{bu}_2\text{dtc})_3]^+$ was used as a standard for calculation. Furthermore the calculated values of the Ni—Se stretching frequencies correspond to the absorption bands found in the spectrum of nickel tris(*N,N*-di-*n*-butyl-diselenocarbamato) bromide.

Though we do not imply these frequencies to be of pure metal chalcogen character, the agreement suggests similar pseudo-octahedral structures for the tris-dithiocarbamato ions of nickel, palladium and platinum.

Table II

M—S stretching frequencies of $[\text{M}(\text{bu}_2\text{dtc})_3]^+$ and M—Se stretching frequencies of $[\text{Ni}(\text{bu}_2\text{dsc})_3]^+$ in cm^{-1} .

Calculated values of M—S and M—Se with $[\text{Pd}(\text{bu}_2\text{dtc})_3]^+$ as a standard, are given in parentheses.

$[\text{Ni}(\text{bu}_2\text{dtc})_3]^+$	$[\text{Pd}(\text{bu}_2\text{dtc})_3]^+$	$[\text{Pt}(\text{bu}_2\text{dtc})_3]^+$	$[\text{Ni}(\text{bu}_2\text{dsc})_3]^+$
410 (417)	383	365 (362)	327 (327)
387 (392)	360	341 (341)	317 (308)
370 (362)	333	(315)	284 (284)

The magnetic measurements of the platinum compounds $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+[\text{CuCl}_2]^-$, $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+[\text{CuBr}_2]^-$ and $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+[\text{AuBr}_2]^-$ reveal high momentums, which are nearly temperature independent.

Table III

Molar magnetic susceptibilities X_m in cgs units of some platinum bis(*N,N*-di-*n*-butyldithiocarbamato) compounds, corrected for diamagnetism.

	T = 293 °K	T = 113 °K
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuCl}_2$	$665 \cdot 10^{-6}$	$755 \cdot 10^{-6}$
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuBr}_2$	$804 \cdot 10^{-6}$	$955 \cdot 10^{-6}$
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{AuBr}_2$	$459 \cdot 10^{-6}$	$461 \cdot 10^{-6}$

More often we found complexes of nickel, palladium and platinum with dithiocarbamato ligands to have such a high susceptibility. This phenomenon is currently under investigation.

The NMR spectra of the platinum compounds investigated, measured at different temperatures, show remarkable similarity to those of $[\text{Ni}(\text{bu}_2\text{dtc})_3]^+\text{Br}^-$, giving evidence that in the platinum compounds the ligand is also present as dithiocarbamate and not as thiuram disulfide¹³. τ -values are given in Table IV.

Table IV

NMR proton resonances. τ in ppm. Temperature 33°

	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—N}$			
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuCl}_2$	8.56	8.12	7.80	5.96
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{CuBr}_2$	8.56	8.12	7.78	5.94
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{AuBr}_2$	8.56	8.14	7.80	5.94
$\text{Pt}(\text{bu}_2\text{dtc})_3\text{I}_3^9$	8.58	8.14	7.80	5.97
$\text{Ni}(\text{bu}_2\text{dtc})_3\text{Br}$	8.72	8.30	7.98	6.08

¹³ A. Avdeef, J. P. Fackler Jr. and R. G. Fischer Jr., J. Am. Chem. Soc. **92**, 6972 (1970).

Molar conductivity measurements show the complexes to be 1:1 electrolytes. The values found for Λ_0 are given in Table V. The dependence of the molar conductivity on the square root of the concentration

gives a straight line. The slope of this line, $A = \frac{\Lambda_0 - \Lambda}{\sqrt{c}}$ is characteristic

of this type of electrolytes. From the relation $A = \alpha\Lambda_0 + \beta$, with $\alpha = 0.779$ and $\beta = 44.2^{14}$ at 25° , theoretical values can be computed. The experimental and calculated values, including the data for $\text{Pt}(\text{bu}_2\text{dtc})_3\text{Br}$ are given in Table V.

Table V

Conductivity data in nitrobenzene at 25°C .
 Λ_0 in $\Omega^{-1} \text{cm}^2 \text{mole}^{-1}$.

	Λ_0	A_{exp}	A_{calc}
$[\text{Pt}(\text{bu}_2\text{dtc})_3]^+ [\text{CuCl}_2]^-$	28.9	56	67
$[\text{Pt}(\text{bu}_2\text{dtc})_3]^+ [\text{CuBr}_2]^-$	28.2	55	67
$[\text{Pt}(\text{bu}_2\text{dtc})_3]^+ [\text{AuBr}_2]^-$	29.6	62	68
$[\text{Pt}(\text{bu}_2\text{dtc})_3]^+ \text{Br}^-$ ⁹	28.8	66	67

From Λ_0 of $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+ \text{Br}^-$ and λ_0^- of Br^- ($21.9 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$) the equivalent conductivity of the $[\text{Pt}(\text{bu}_2\text{dtc})_3]^+$ ion, λ_0^+ , can be calculated. This value 6.9 is higher than the one calculated for the $[\text{Ni}(\text{bu}_2\text{dtc})_3]^+$ ion (3.5)⁶. This discrepancy is not very serious in view of the normal error in the measurements. The λ_0^- values of $[\text{CuCl}_2]^-$, $[\text{CuBr}_2]^-$ and $[\text{AuBr}_2]^-$ are 22.0, 21.5 and 22.7, respectively. The λ_0^- value for $[\text{AuBr}_2]^-$ in $[\text{Au}(\text{bu}_2\text{dtc})_2]^+ [\text{AuBr}_2]^-$ is found to be 21.0^{15} .

From the results reported, the general conclusion can be drawn that the compounds of the type $[\text{M}(\text{R}_2\text{dtc})_3]^+ \text{X}^-$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) can be prepared from $\text{M}(\text{R}_2\text{dtc})_2$ in various ways. The type of anion depends on the metal and the oxidant used. The $[\text{Pd}(\text{R}_2\text{dtc})_3]^+$ and $[\text{Pt}(\text{R}_2\text{dtc})_3]^+$ ions seem to be isostructural with $[\text{Ni}(\text{R}_2\text{dsc})_3]^+$ ¹⁶ and

¹⁴ E. G. Taylor and C. A. Kraus, J. Am. Chem. Soc. **69**, 1731 (1947).

¹⁵ J. G. M. van der Linden, Rec. Trav. Chim. **90**, 1027 (1971).

¹⁶ P. T. Beurskens and J. A. Cras, J. Cryst. Mol. Struct. **1**, 63 (1971).

$[\text{Ni}(\text{R}_2\text{dte})_3]^{+15}$ in which the Ni atom is octahedrally coordinated with 6 Se and 6 S atoms, respectively, as is revealed by X-ray studies.

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