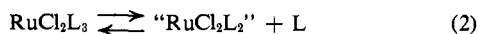
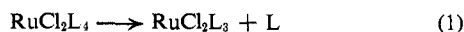


Figure 1. The 40.5-MHz ^{31}P nmr spectra of (a) $\text{RuCl}_2(\text{PPh}_3)_4$ in CHCl_3 at 30° , (b) $\text{RuCl}_2(\text{PPh}_3)_3$ in CHCl_3 at 30° , and (c) $\text{RuCl}_2(\text{PPh}_3)_3$ in CHCl_3 at -90° . Horizontal bar extends from 0 to +5 ppm.

more intense resonance of RuCl_2L_4 . In addition, free PPh_3 is present. Finally, an extremely broad resonance is observed at -57.3 ppm with intensity twice that of the PPh_3 signal. These spectra are consistent with the following reactions⁶



RuCl_2L_4 dissociates essentially completely to RuCl_2L_3 , which produces the resonance at -41.1 ppm. This five-coordinate unsaturated complex then further dissociates to some extent to produce what might be a 14-electron species (eq 2).

The solid-state structure of RuCl_2L_3 is unusual.⁷ While MX_2L_3 species are usually trigonal bipyramidal with all phosphines equatorial,⁸ RuCl_2L_3 is square pyramidal with two trans basal phosphines and the third phosphine apical. The apical phosphorus-ruthenium bond is 0.16 \AA (20σ) shorter than the average basal Ru-P bond length. Since the ^{31}P spectrum at 30° is not the AX_2 pattern expected for square pyramidal RuCl_2L_3 , the question of structural change on dissolution immediately arises. Alternatively, square pyramidal geometry may persist in solution; bending motions even more subtle than those required for Berry pseudorotation might render the phosphines time-average equivalent. Finally, equivalence could result from intermolecular exchange.

The ^{31}P nmr spectrum of RuCl_2L_3 at -90° in CH_2Cl_2 (Figure 1c) shows that the phosphine ligands are inequivalent in solution. The major peaks constitute an AX_2 pattern with $J_{\text{P-P}'} = 30$ Hz. The population-weighted average of the two chemical shifts is -41.2 ppm. Although *o*-phenyl hydrogen interactions have been discussed,⁷ we believe that the square pyramidal geometry observed in solution is determined by electronic requirements of the d^6 configuration. Low-spin d^6 complexes are predicted to be square pyramidal using second-order Jahn-Teller arguments.⁹

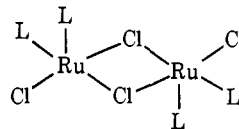
(6) All solutions were approximately $0.1 M$.

(7) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(8) B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Rev. Sci. Phys. Chem. (Ser. 1)*, **11**, 33 (1972).

(9) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

The low temperature spectrum of RuCl_2L_3 ($0.1 M$) also shows about 5 mol % of "RuCl₂L₂." The AB pattern observed for this species is inconsistent with a 14-electron monomer. Tetrahedral or cis or trans planar species would show a ^{31}P singlet. A halide bridged dimer, $[\text{RuCl}_2\text{L}_2]_2$ (below), accounts for the observed spectrum. This dimer maintains square pyramidal geometry about ruthenium.



These results explain the interchangeability of RuCl_2L_3 and RuCl_2L_4 in synthetic procedures. Moreover, the equilibria underlying the production of $\text{L}_2\text{ClRu}(\text{Cl})_3\text{-Ru}(\text{N}_2)\text{L}_2$ from RuCl_2L_4 by reverse osmosis¹⁰ are now demonstrated directly. In fact, an elementary procedure suffices to remove phosphine from RuCl_2L_3 . If RuCl_2L_3 is slurried in refluxing ethanol the solid darkens. The solvent extracts triphenylphosphine, leaving a solid of formula RuCl_2L_2 which is insoluble in CHCl_3 .¹¹ The behavior of the $\text{Ru}(\text{II})\text{-PPh}_3$ system is similar to that of the $\text{RhCl}(\text{PPh}_3)_3\text{-Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ equilibrium.¹² Although the dimer observed here differs structurally from the $\text{Ru}_2\text{Cl}_3\text{L}_6^+$ cations formed by mixed aryl alkyl phosphines,¹³ there is a clear tendency for $\text{Ru}(\text{II})$ phosphine complexes to form halogen bridges.

Although phosphorus-phosphorus coupling simplifies identification of species present in solution, it must be noted that most resonances observed here are exchange broadened. We are presently attempting to obtain thermodynamic and kinetic data for all inter- and intramolecular processes.¹⁴

Acknowledgment is made to the National Science Foundation for support under Grant No. GP-38641X.

(10) L. W. Gosser, W. H. Knoth, and G. W. Parshall, *J. Amer. Chem. Soc.*, **95**, 3436 (1973).

(11) Compare ref 3; see also R. K. Poddar and U. Agarwala, *J. Inorg. Nucl. Chem.*, **35**, 567 (1973).

(12) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 3240 (1972).

(13) M. S. Lupin and B. L. Shaw, *J. Chem. Soc. A*, 741 (1968), and references therein.

(14) A referee called our attention to a quantitative study of reaction 2: B. R. James and L. D. Markham, Abstract 58, 6th International Conference on Organometallic Chemistry, Amherst, Mass., 1973. See also B. R. James and L. D. Markham, *Inorg. Chem.*, **13**, 97 (1974).

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Synthesis of 1,2-Dithiosquarate Salts and X-Ray Crystal Structure of Potassium Bis(dithiosquarato)nickelate(II)

Sir:

The oxocarbon anions have been recognized as an aromatic series,¹ and a nitrogen analog (2) of the squarate dianion (1) has been reported.² Our interest

(1) R. West and J. Niu, "Non-Benzenoid Aromatics," Vol. 1, Academic Press, New York, N. Y., 1969, p 312.

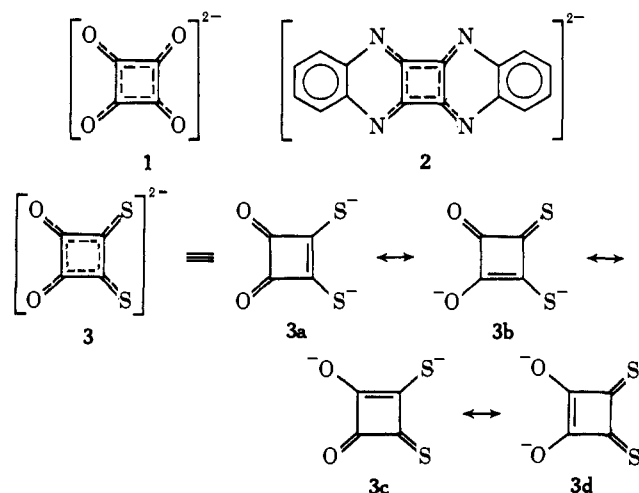
(2) S. Hunig and H. Pütter, *Angew. Chem., Int. Ed. Engl.*, **12**, 149 (1973).

Table I. Analytical Data for Some Compounds Containing the Dithiosquarate Anion

Compound	% C calcd (obsd)	% H calcd (obsd)	% X calcd (obsd)	Color
Na ₂ S ₂ C ₄ O ₂ · 2.67H ₂ O	20.16 (20.17)	2.03 (2.25)	S 26.92 (26.81) O 31.36 (31.33)	Yellow
K ₂ S ₂ C ₄ O ₂ · H ₂ O	19.99 (19.89)	0.84 (0.89)		Yellow
K ₂ Ni(S ₂ C ₄ O ₂) ₂ · H ₂ O	21.68 (21.24)	0.45 (0.43)		Red-brown
K ₂ Zn(S ₂ C ₄ O ₂) ₂ · 2H ₂ O	20.53 (20.40)	0.86 (0.98)		Yellow
(Bu ₄ N) ₂ Ni(S ₂ C ₄ O ₂) ₂ ^a	57.74 (57.66)	8.72 (8.91)	N 3.37 (3.15)	Red-brown
(BzPh ₃ P) ₂ Zn(S ₂ C ₄ O ₂) ₂ ^b	65.68 (65.23)	4.18 (4.12)		Yellow
(BzPh ₃ P) ₂ Cu(S ₂ C ₄ O ₂) ₂	65.80 (65.74)	4.19 (4.18)	Cu 6.00 (6.13)	Dark green

^a Bu₄N = tetra-*n*-butylammonium cation. ^b BzPh₃P = benzyltriphenylphosphonium cation.

in synthesizing sulfur-substituted analogs of the oxocarbons as well as in the possibilities of S,S', S,O, and O,O' chelation in the 1,2-dithiosquarate dianion (3) led us to consider the synthesis of this hitherto unknown species.³



Some of the chemistry of the 1,2-dithiosquarate dianion is summarized in Scheme I. The 1,2-dithiosquarate dianion is prepared from diethyl squarate (4), which can be obtained either by reaction of perchlorocyclobutenone with ethanol in a modification of a procedure of Maahs⁴ or by ethanol esterification of squaric acid.⁵ On addition of diethyl squarate to sodium or potassium hydrosulfide in alcohol, the dithiosquarate salts are formed in high yields as bright yellow precipitates which can be recrystallized from aqueous ethanol or methanol. Disodium 1,2-dithiosquarate has also been prepared in low yield ($\leq 10\%$) from 5, the bis(cyclohexylamide) of squaric acid, by the amide cleavage method of Shahak and Sasson.⁶ The ir spectrum of the sodium salt shows two strong absorptions at 1710 and 1620 cm^{-1} and the potassium salt at 1700 and 1625 cm^{-1} which can be attributed to C=O stretching vibrations. The electronic spectrum of the anion in aqueous solution shows peaks at 346, 325 (sh), 250, and 230 nm.

Anionic complexes of 1,2-dithiosquarate with transition metals can be formed by reaction with $1/n$ equivalents of the n -valent metal cation. The potassium

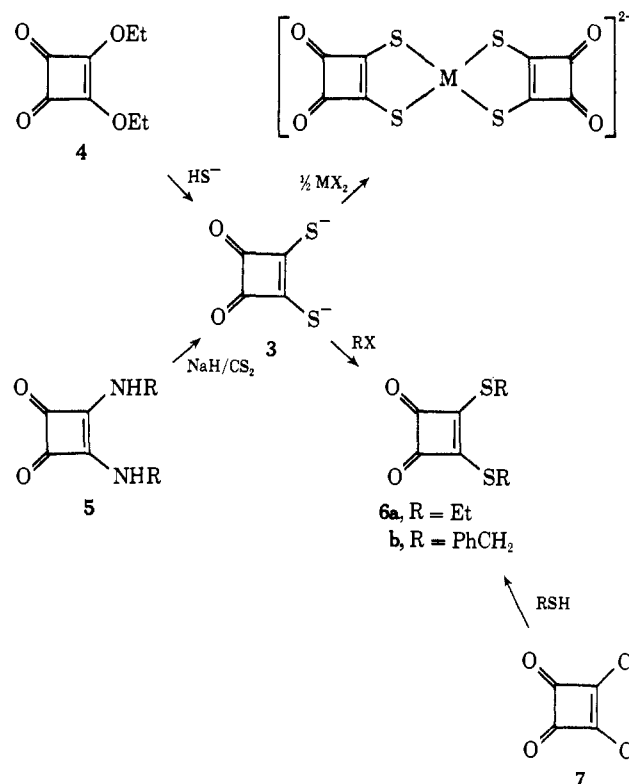
(3) A preliminary account of some of this work has been reported: D. Coucouvanis and F. J. Hollander, paper presented at 9th Midwest Regional Meeting of the American Chemical Society, Lawrence, Kan., Oct 1973.

(4) G. Maahs, *Justus Liebigs Ann. Chem.*, **686**, 55 (1965).

(5) G. Maahs and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, **5**, 888 (1966).

(6) I. Shahak and J. Sasson, *J. Amer. Chem. Soc.*, **95**, 3440 (1973).

Scheme I. Synthesis and Derivatives of the 1,2-Dithiosquarate Dianion



salts of the bis(dithiosquarate)nickelate(II) and -zincate(II) have been isolated from concentrated aqueous solutions and quaternary cation salts have been precipitated from aqueous solution and recrystallized from nonaqueous media (e.g., dichloromethane-ether). Benzyltriphenylphosphonium bis(dithiosquarate)cuprate(II) was prepared by treating the corresponding zinc complex with anhydrous cupric chloride in acetone. The analytical data for the reported compounds are given in Table I.⁷

In the transition metal complexes, the carbonyl absorptions are shifted to slightly higher frequencies (1750–1655 cm^{-1}), suggesting that the anion is bonded to the metal through sulfur. To confirm this mode of bonding as well as the formulation of the ligand as the 1,2-dithiosquarate dianion, the X-ray crystal structure of potassium bis(dithiosquarate)nickelate(II) dihydrate was determined and is shown in Figure 1. The nickel atom, on a crystallographic center of symmetry, is coordinated in a planar fashion by the sulfur atoms of two

(7) In addition to the complexes reported in this communication, complexes with several other metals have been isolated and are presently being characterized.

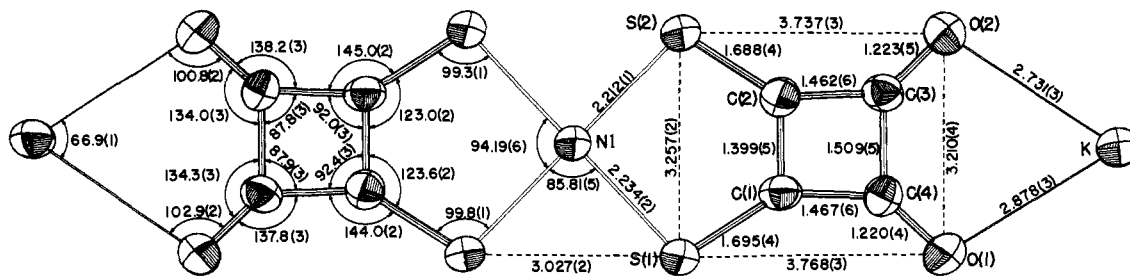
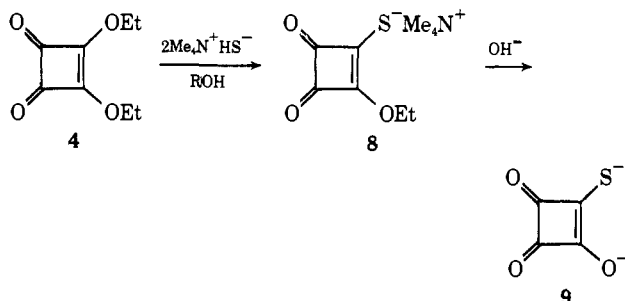


Figure 1. The molecular structure of $K_2Ni(S_2C_4O_2)_2 \cdot 2H_2O$ ($R_1 = 0.018$). The nickel atom sits on a crystallographic center of symmetry. Distances are in ångströms and angles in degrees. The figures in parentheses represent the estimated standard deviation of the least significant digit(s). Water molecules and complete coordination of the potassium have been left out for clarity. The thermal ellipsoids as plotted by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

ligands and shows no axial interactions. The ligand itself is very closely planar, and this plane is essentially coplanar with that of the NiS_4 moiety. The exterior angles of the two carbon atoms attached to sulfur are highly distorted from the "ideal" value of 135° to reduce the sulfur-sulfur bite distance to its observed value of 3.26 Å. The quite large oxygen-oxygen bite distance of 3.21 Å, however, is essentially unperturbed. The carbon-carbon, carbon-sulfur, and carbon-oxygen bond lengths are compatible with a description of the anion that gives greatest weight to resonance form **3a** with significant contributions from **3b** and **3c**.⁸ The potassium atoms are irregularly coordinated by oxygens from several ligands and by the water molecules.

Reaction of dipotassium 1,2-dithiosquarate with ethyl iodide in DMF-water yields *S,S'*-diethyl 1,2-dithiosquarate (**6a**). The ir spectrum (CCl_4) shows strong bands at 1770, 1745, 1455, and 1135 cm^{-1} . The mass spectrum shows a strong parent ion peak at 202 m/e , and the nmr spectrum is typical of S-bonded ethyl esters (δ 3.46 and 1.48 ppm with respect to TMS). A similar ester (**6b**) has been prepared by reaction of benzyl mercaptan and 3,4-dichlorocyclobutenedione (**7**).

When diethyl squarate is treated with an alcoholic solution of 2 equiv of tetramethylammonium hydroxide saturated with hydrogen sulfide, displacement of only one ethoxy group occurs, yielding the *O*-ethyl monothiosquarate anion (**8**). The ir spectrum of this anion



shows strong bands at 1760 and 1670 cm^{-1} . The electronic spectrum shows a single peak at 320 nm. The nmr spectrum in acetonitrile shows a quartet at δ 4.80 (2 H), a singlet at δ 3.15 (12 H), and a triplet at 1.38 (3 H). Hydrolysis of the *O*-ethyl monothiosquarate anion appears to give the monothiosquarate dianion (**9**), isolable as the bis(tetramethylammonium),

(8) Full details on the chelation chemistry of the dithiosquarate dianion and the crystal structure of the nickel complex will be given in a subsequent paper. F. Hollander and D. Coucouvanis, manuscript in preparation.

-dipotassium, and -barium salts. Characterization and study of dianion **9** is currently being carried out.

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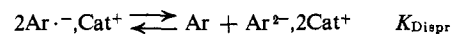
R. West, D. Eggerding
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received January 26, 1974

Disproportionation of the Lithium, Sodium, and Potassium Salts of Anthracenide and Perylenide Radical Anions in DME and THF

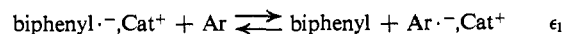
Sir:

Our recent studies of protonation of Li^+ , Na^+ , and K^+ salts of radical anions of anthracene^{1,2} and of perylene³ in THF or DME demonstrated the important role of dianions in the overall process. The evaluation of the results required knowledge of the respective disproportionation constants



and to provide the necessary data we carried out potentiometric titrations of the pertinent hydrocarbons in the above solvents.

The potentiometric titrations, originally developed by Hoiijtink, *et al.*,⁴ and subsequently improved in our laboratory,⁵ yield the standard potentials ϵ_1 and ϵ_2 of the following equilibria⁶



(1) A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, **95**, 659 (1973).

(2) A. Rainis, R. Tung, and M. Szwarc, *Proc. Roy. Soc.*, in press.

(3) G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).

(4) G. J. Hoiijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, **75**, 487 (1956).

(5) J. Jagur-Grodzinski, M. Feld, G. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(6) The directly measured potentials ϵ_1 and ϵ_2 refer to the reactions of ion pairs and of the associates such as $Ar^{2-}, 2Cat^+$ because the dissociations, $Ar^{\cdot-}, Cat^+ \rightleftharpoons Ar^{\cdot-} + Cat^+$ and $Ar^{2-}, 2Cat^+ \rightleftharpoons Ar^{2-}, Cat^+ + Cat^+$, are negligible under conditions prevailing in the titrations performed in THF or DME.