Transition Metal Complexes of the *cis*-Dithiosquaramide Ligand Family

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3,4-Bis(alkylamino)-3-cyclobuten-1,2-dithiones (*cis*-dithiosquaramides, LH_2) react with divalent metal acetates to give neutral 2:1 complexes of the general formula $M^{II}(LH)_2\cdot xH_2O$ (M^{II} = Ni, Cu, Pd). The ligands bind in a didentate S_2 fashion forming a square planar $M^{II}S_4$ coordination sphere. Spectral data suggest that complexation localizes the ligand's electronic structure into a more dithiolene–diimine-like form, and the crystal structure of $Pd(dcy\text{-}DTSQ)_2\cdot 2H_2O$ (dcy-DTSQ = 3,4-bis(cyclohexylamino)-3-cyclobuten-1,2-dithionato ligand) provides further evidence to support this suggestion. The compound $Pd(dcy\text{-}DTSQ)_2\cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/a$ (No. 14) with cell dimensions $a = 10.222$ (3) Å, $b = 16.015$ (3) Å, $c = 11.664$ (1) Å, $\beta = 110.25$ (1)°, and $V = 1791.4$ (7) Å^3. For $Z = 2$ and a formula weight = 757.42, the calculated density is 1.403 g/cm^3. Diffraction data (Cu Kα) were collected with a Rigaku AFC5R diffractometer at 21 °C, and the structure was solved by direct methods. The agreement factors were $R = 0.030$ and $R_w = 0.044$ for the 2076 observed reflections.

Introduction

3,4-Dihydroxy-3-cyclobuten-1,2-dione (squaric acid) and, in particular, its conjugate base (squarate anion, $C_4O_4^{2-}$) have given rise to interesting and varied coordination chemistry. Commonly, squarate complexes form one-dimensional polymers with squarate ligands bridging between metal centers in either O^1,O^2 or O^1,O^3 modes[1] or as bridged dimeric species.[2] Coordination of squarate through all four oxygen atoms has also been observed.[3] Chelation to a single metal has been observed, for example, in $[Ce(H_2O)_2](C_4O_4)_3$,[4] and incorporation into polyoxoanions, such as $[\{Mo_3O_8(OMe)\}(C_4O_4)_2]^{3-}$, has been reported.[5] A hydrogen squarate containing polyoxoanion of formula $[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$ has been described.[6] Recently six new copper(II) squarate complexes were reported, including examples having one-dimensional chains with squarate bridging between Cu^{II} complex units in a μ-O^1,O^2 mode, two-dimensional networks with squarate acting as a tris-O^1,O^2,O^3-monodentate ligand, binuclear μ-O^1,O^3-squarate Cu^{II} complexes, and monodentate squarate coordination in a mononuclear complex.[1f]

Numerous derivatives of squaric acid are known,[7] and of these both *cis*-dithiosquarate ($C_4O_2S_2^{2-}$) and tetrathiosquarate ($C_4S_4^{2-}$) have been examined as ligands toward the transition elements. For dithiosquarate many discrete 2:1 complexes are known, and among the structurally characterized examples are $K_2[Ni(C_4O_2S_2)_2]$,[8] two salts of $[Pd(C_4O_2S_2)_2]^{2-}$,[9] and the tetrahedral complex $(Ph_4P)_2[Fe(C_4O_2S_2)_2]$.[10] In $[Cu(en)_2][Cu(C_4O_2S_2)_2]$, the bis(dithiosquarato)copper(II) anion exists as a discrete 2:1 complex in the solid state, whereas the copper(I) dithiosquarate complex in $[Cu(en)_2(H_2O)]_2[Cu_4(C_4O_2S_2)_4]\cdot 2H_2O$ exists as a tetramer.[11] A metallocubane structure is observed in the Cu^I derivative $(Ph_4P)_4[Cu_8(C_4O_2S_2)_6]$.[12] A dimeric oxomolybdenum species $(\mu\text{-}O)(\mu\text{-}S)[(M{=}O)(C_4O_2S_2)]_2$ is also known.[13]

The versatility of the tetrathiosquarato ligand has been demonstrated largely through the efforts of Beck et al.[14] Discrete complexes having one tetrathiosquarato ligand bridging between two metal centers in a bis-didentate arrangement are known, and some examples include $Rh(cod)(C_4S_4)Rh(cod)$ (cod = 1,4-cyclooctadiene), $[Cr(CO)_4(C_4S_4)Cr(CO)_4]^{2-}$, and $Au(Me)_2(C_4S_4)Au(Me)_2$.[14] Reaction of various transition metal species with $C_4S_4^{2-}$ in water afforded polymers of the formulas $(M_2C_4S_4)_n$ (M^I = Cu, Ag, Au) and $(MC_4S_4)_n$ (M^{II} = Cu, Zn, Cd, Hg, Fe, Co, Ni, Pd, Pt, Sn, Pb), which are believed to have chain structures.[14a,c] The structure of the discrete 2:1 complex $(Ph_4As)_2[Ni(C_4S_4)_2(py)_2]\cdot 2py$ (py = pyridine) has been solved and shows the tetrathiosquarato ligands bound in a chelating didentate fashion.[14c]

Despite the extensive studies on the coordination chemistry of squarate and its dithio and tetrathio derivatives, little work has been reported on other derivatives of squaric acid and in particular the dithiosquaramides. Dithiosquaramides are known in both cis and trans forms. The cis form is particularly interesting because it has the potential to coordinate in several different fashions including S,S′-chelation, N,N′-chelation, or N,S-chelation. One can also envision chain structures with dithiosquara-

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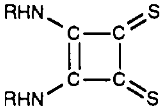

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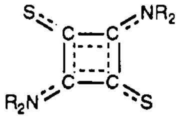

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mide ligands bridging between metal centers in either a bis-N,S mode or an N,N′-S,S′ mode. In this work we detail what, to our knowledge, are the first studies on the coordination chemistry of *cis*-dithiosquaramide ligands.[15]

Experimental Section

cis-Di-*n*-butylsquarate was prepared from squaric acid (Aldrich) as described by Maahs[16] and used as a solution in 1-butanol. *cis*-Dicyclohexylsquaramide (dcy-SQ) (mp = 318–323 °C dec), *cis*-dicyclopentylsquaramide (dcp-SQ) (mp > 320 °C, darkens above 250 °C), and *cis*-di-*n*-butylsquaramide (dbu-SQ) (mp = 254–256 °C dec) were prepared by stoichiometric reaction of *cis*-di-*n*-butylsquarate and the appropriate amine in refluxing 1-butanol.[17] The *cis*-squaramides were characterized by elemental analysis[18] and electron-impact mass spectroscopy (parent ion observed for each). Dichloromethane was distilled from P_4O_{10}. P_4S_{10} (Aldrich), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were used as received.

Mass spectra were recorded by staff at the University of Kansas using a Ribermag R10-10 mass spectrometer for electron impact (EI) and a VG Analytical Ltd. ZAB HS mass spectrometer for fast atom bombardment (FAB) (magic bullet[19] or *m*-nitrobenzyl alcohol matrix). Infrared spectra were obtained by using a Perkin-Elmer 1600 series Fourier transform spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on either a GE QE-300 Plus or a Varian XL 300 spectrometer, each operating at about 300 MHz for ^1H and 75 MHz for ^{13}C, and were referenced to residual solvent resonances or TMS. Electronic spectra were recorded using either a Varian 2300 UV-vis or Hewlett-Packard 8452A diode-array spectrophotometer. Elemental analyses were performed either by Galbraith Laboratories, Inc., or by staff in the Analytical Laboratory at the University of Kansas.

3,4-Bis(cyclohexylamino)-3-cyclobuten-1,2-dithione, dcy-DTSQ.[20] Excess P_4S_{10} (1.7 g) and dcy-SQ (1.7 g, 6.2 mmol) were suspended in dry dichloromethane (70 mL), and the mixture was stirred at 25 °C for 16 h. Ethanol (10 mL) was added to the resulting dark red reaction mixture to destroy unreacted P_4S_{10}. Because of the presence of a gummy residue, very thorough mixing with a spatula was required. The red color quickly dissipated, and the remaining brown solid was collected, washed with ca. 40 mL of ethanol and then extensively with diethyl ether, and briefly dried in air. The crude product was recrystallized three times from DMSO to give dcy-DTSQ as yellow-brown platelets. The recrystallized product was washed with ethanol and diethyl ether and dried in vacuo. Yield: 0.98 g, 3.2 mmol, 52%.

EI mass spectrum (*m/z*): 308 (M), 225 ($M - C_6H_{11}$), and other ions. Anal. Calcd for $C_{16}H_{24}N_2S_2$: C, 62.29; H, 7.84; N, 9.08. Found: C, 62.00; H, 7.98; N, 9.00 UV-vis (*N,N*-dimethylformamide): λ_{max} (log ϵ) = 392 (4.71), 361 (shoulder), 277 (4.43) nm. UV-vis (methanol): λ_{max} = 385, 357 (shoulder), 274 nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1710, 1569 cm^{-1}.

3,4-Bis(cyclopentylamino)-3-cyclobuten-1,2-dithione, dcp-DTSQ. Conditions were similar to those described for dcy-DTSQ above. Starting quantities were dcp-SQ (0.52 g, 2.1 mmol), P_4S_{10} (0.6 g), and dichloromethane (50 mL). Reaction time was 40 min. After destruction of unreacted P_4S_{10} with ethanol (5 mL), the crude product was recovered by filtration and then recrystallized from DMSO/ethanol to give dcp-DTSQ as yellow-brown platelets. The recrystallized product was washed with ethanol, washed freely with diethyl ether, and dried in vacuo. Yield: 0.24 g, 0.86 mmol, 41%.

EI mass spectrum (*m/z*): 280 (M), 211 ($M - C_5H_9$), and other ions. Anal. Calcd for $C_{14}H_{20}N_2S_2$: C, 59.96; H, 7.19; N, 9.99. Found: C, 60.10; H, 7.49; N, 10.00 UV-vis (methanol): λ_{max} = 386, 357 (shoulder), 275 nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1708, 1572 cm^{-1}.

3,4-Bis(*n*-butylamino)-3-cyclobuten-1,2-dithione, dbu-DTSQ.[21] Conditions for the synthesis of dbu-DTSQ were similar to those described for dcy-DTSQ above. Owing to its higher solubility, however, the isolation of dbu-DTSQ was different from that of the other two ligands. For the quantities dbu-SQ (0.468 g, 2.09 mmol), P_4S_{10} (0.41 g), and dichloromethane (40 mL), and a total reaction time of 3 h, the resulting reaction mixture, consisting of a red solution and a gummy red residue, was treated as follows: (i) ethanol (10 mL) added; (ii) volatiles removed by rotary evaporation; (iii) residue suspended in ethanol (10 mL); (iv) water (10 mL) added to suspension; (v) collected and dried the yellow crude product; (vi) chromatographed the crude product on silica gel using chloroform/DMF (20/1) as eluent. Recrystallization from chloroform/petroleum ether gave dbu-DTSQ as a yellow crystalline material. Yield: 0.294 g, 1.15 mmol, 55%.

EI mass spectrum (*m/z*): 256 (M), 199 ($M - C_4H_9$), and other ions. Anal. Calcd for $C_{12}H_{20}N_2S_2$: C, 56.21; H, 7.86; N, 10.92. Found: C, 56.27; H, 7.85; N, 10.68. UV-vis (chloroform): λ_{max} = 386 (4.40), 361 (shoulder), 276 (4.18) nm. ^1H NMR (chloroform-*d*): δ 0.921 (t, 6 H, CH_3), 1.414 (m, 4 H, CH_2), 1.678 (m, 4 H, CH_2), 4.093 (broad, 4 H, CH_2), 8.688 (broad, 2 H, NH). ^{13}C NMR (chloroform-*d*): δ 201.60 (C=S), 170.26 (C=N), 44.17 (CH_2–N), 32.80 (CH_2), 19.65 (CH_2), 13.68 (CH_3). IR (KBr, region from 1800 and 1500 cm^{-1}): 1723, 1608 cm^{-1}.

Ni(dbu-DTSQ)$_2$. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (34.6 mg, 0.139 mmol) in warm DMF (10 mL) was added to a solution of dbu-DTSQ (66.4 mg, 0.259 mmol) in warm DMF (5 mL). A dark red solution formed immediately. After several minutes, water was added dropwise until significant turbidity was evident (3 mL total). The mixture was then cooled and stored at 4 °C. The orange-red product thus obtained was collected by filtration, washed with water, briefly dried in vacuo, recrystallized from methanol/dichloromethane, and dried in vacuo for several days. Yield: 54 mg, 0.0948 mmol, 73%.

Positive ion FAB mass spectrum (*m/z*): 569 (100%, $M(LH)_2 + H$), 314 (32, $M(LH_2)$). Anal. Calcd for $C_{24}H_{38}N_4S_4Ni$: C, 50.61; H, 6.73; N, 9.84. Found: C, 50.30; H, 6.90; N, 9.74. UV-vis (chloroform): λ_{max} (log ϵ) = 492 (3.94), 388 (4.21), 334 (shoulder), 320 (4.57), 272 (4.45) nm. ^1H NMR (chloroform-*d* with a small amount of methanol-d_4 added): δ 0.872 (t, 6 H, CH_3), 1.31 (m, 4 H, CH_2), 1.53 (m, 4 H, CH_2), 3.30 (s, "NH"), 3.50 (t, CH_2). ^{13}C NMR (chloroform-*d* with a small amount of methanol-d_4 added): δ 13.51 (CH_3), 19.75 (CH_2), 32.57 (CH_2), 46.59 (CH_2–N), 159.17 (C=N), 193.23 (C=S). IR (KBr, region from 1800 to 1500 cm^{-1}): 1713, 1651 cm^{-1}.

Ni(dcy-DTSQ)$_2$·2.5H$_2$O. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (119.0 mg, 0.478 mmol) in warm DMSO (6 mL) was added to dcy-DTSQ (295.3 mg, 0.957 mmol) in hot (ca. 115 °C) DMSO (6 mL). A dark red solution formed immediately. The solution was cooled to 25 °C and stirred for 12 h. The crude product, which deposited as a dark red-brown solid, was collected by filtration, washed with DMSO (10 mL), and recrystallized several times from THF/*n*-heptane to give $Ni(dcy\text{-}DTSQ)_2 \cdot 2.5H_2O$ as a dark red crystalline material. Yield: 152.2 mg, 0.212 mmol, 44%.

Positive ion FAB mass spectrum (*m/z*): 673 (100%, $M(LH)_2 + H$), 366 (53, $M(LH_2)$). Anal. Calcd for $C_{32}H_{51}N_4NiO_{2.5}S_4$: C, 53.48; H, 7.15; N, 7.80. Found: C, 53.29; H, 7.12; N, 7.49. UV-vis (chloroform): λ_{max} (log ϵ) = 492 (4.12), 388 (4.40), 320 (4.78), 276 (4.66) nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1712, 1637 cm^{-1}.

Ni(dcp-DTSQ)$_2$·2H$_2$O. This complex was prepared in a manner similar to that for Ni(dcy-DTSQ)$_2$. The crude product precipitated from the DMSO reaction solution upon cooling and was recrystallized (twice) from dichloromethane/*n*-heptane to give $Ni(dcp\text{-}DTSQ)_2 \cdot 2H_2O$ as a dark

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(15) The *cis*-dithioaquaramide ligands in this study are abbreviated dcy-DTSQ, dcp-DTSQ, and dbu-DTSQ, where the lower case letters refer to the substituents on N and N′ (dcy = *N,N′*-dicyclohexyl-, dcp = *N,N′*-dicyclopentyl-, dbu = *N,N′*-di-*n*-butyl-). The same abbreviations are used whether the ligand is coordinated or uncoordinated, though the coordinated form is deprotonated (LH^-) and the uncoordinated form is not (LH_2).

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(17) Maahs, G.; Hegenberg, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 888. They reported dcy-SQ (mp = 314–323 °C) and dbu-SQ (mp = 252–255 °C).

(18) Anal. Calcd for $C_{16}H_{24}N_2O_2$ (dcy-SQ): C, 69.53; H, 8.75; N, 10.14. Found: C, 69.58; H, 9.00; N, 10.00. Calcd for $C_{14}H_{20}N_2O_2$ (dcp-SQ): C, 67.72; H, 8.12; N, 11.28. Found: C, 67.50; H, 8.40; N, 10.82. Calcd for $C_{12}H_{20}N_2O_2$ (dbu-SQ): C, 64.26; H, 8.99; N, 12.49. Found: 63.92; H, 8.99; N, 11.99.

(19) A dithioerythritol/dithiothreitol mixture.

(20) (a) Reference 16 reported dcy-DTSQ but provided no experimental details. (b) Eggerding, D.; West, R. J. *Org. Chem.* **1976**, *41*, 3904. They reported the synthesis of dcy-DTSQ in hexamethylphosphoric triamide solvent.

(21) Seitz, G.; Mann, K.; Schmiedel, R. *Chem.-Ztg.* **1975**, *99*, 332. They reported dbu-DTSQ but experimental details were limited.

red microcrystalline material. Yield based on dcp-DTSQ (66.4 mg, 0.237 mmol): 28.2 mg, 0.043 mmol, 36%.

Positive ion FAB mass spectrum (*m/z*): 633 (26%), 617 (100, M(LH)$_2$ + H), 338 (49, M(LH$_2$)). Anal. Calcd for $C_{28}H_{42}N_4NiO_2S_4$: C, 51.45; H, 6.48; N, 8.57. Found: C, 52.10; H, 6.98; N, 8.80. IR (KBr, region from 1800 to 1500 cm^{-1}): 1709, 1626 cm^{-1}.

This complex was also prepared using DMF as the solvent. To a solution of dcp-DTSQ (40.6 mg, 0.145 mmol) in warm DMF (3 mL) was added dropwise a solution of $Ni(OAc)_2 \cdot 4H_2O$ (18.6 mg, 0.0747 mmol) in DMF (1.5 mL). A dark red solution resulted, but no precipitate formed even upon storage at −15 °C. Water was then added dropwise until turbidity was evident and the mixture stored at −15 °C. The dark red product was then separated by filtration and dried in vacuo. Analytical data were consistent with the complex being solvated by DMF and water. Yield as Ni(dcp-DTSQ)$_2$·DMF·0.5H$_2$O: 32.3 mg, 0.0462 mmol, 64%. Anal. Calcd for $C_{31}H_{46}N_5NiO_{1.5}S_4$: C, 53.22; H, 6.63; N, 10.01. Found: C, 53.48; H, 6.88; N, 9.98.

Cu(dbu-DTSQ)$_2$·0.5H$_2$O. $Cu(OAc)_2 \cdot H_2O$ (25.7 mg, 0.129 mmol) in warm DMF (10 mL) was added to dbu-DTSQ (65.6 mg, 0.256 mmol) in warm DMF (10 mL). A dark brown solution immediately resulted. After several minutes, water (15 mL) was added whereupon a brown precipitate of the product formed. The product was collected by filtration, washed with water, and dried in vacuo. Yield: 35 mg, 0.0600 mmol, 47%.

Positive ion FAB mass spectrum (*m/z*): 639 (35%), 575 (100, M(LH)$_2$ + 2H), 319 (98, M(LH$_2$)). Anal. Calcd for $C_{24}H_{39}CuN_4O_{0.5}S_4$: C, 49.41; H, 6.74; N, 9.60. Found: C, 49.52; H, 6.78; N, 9.56. UV–vis (chloroform): λ_{max} (log ϵ) = 516 (3.63), 404 (4.39), 322 (4.42), 282 (4.44) nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1709, 1644 cm^{-1}.

Cu(dcy-DTSQ)$_2$·1.5H$_2$O. $Cu(OAc)_2 \cdot H_2O$ (33.4 mg, 0.167 mmol) in DMSO (3 mL) was added to a solution of dcy-DTSQ (89.6 mg, 0.290 mmol) in hot (ca. 100 °C) DMSO (6 mL). A dark brown solution immediately resulted. The reaction mixture was allowed to cool to room temperature and water (30 mL) added to it. The resulting lightly turbid solution was extracted with diethyl ether in two portions (80 mL each). After separation, the ether phase was taken to dryness by rotary evaporation. The brown residue which resulted was recrystallized from toluene/*n*-heptane to give Cu(dcy-DTSQ)$_2$·1.5H$_2$O as a dark brown solid. Yield: 55.3 mg, 0.0784 mmol, 54%.

Positive ion FAB mass spectrum (*m/z*): 743 (10%), 679 (44, M(LH)$_2$ + 2H), 371 (100, M(LH$_2$)). Anal. Calcd for $C_{32}H_{49}CuN_4O_{1.5}S_4$: C, 54.48; H, 7.00; N, 7.94. Found: C, 54.89; H, 6.71; N, 7.18. UV–vis (chloroform): λ_{max} = 386 (shoulder), 326, 280 nm. UV-vis (chloroform/THF, 23:1): λ_{max} = 508 (broad), 396, 318, 283 nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1710, 1589 cm^{-1}.

Cu(dcp-DTSQ)$_2$·1.5H$_2$O. To a solution of dcp-DTSQ (47.7 mg, 0.170 mmol) in DMSO (3 mL) was added $Cu(OAc)_2.H_2O$ (17.8 mg, 0.0892 mmol) in DMSO (3 mL). A dark brown solution resulted immediately. After 30 min a small quantity of solid was evident. Water (6 mL) was added to precipitate additional product. The brown precipitate was then collected, washed with water, and dried in vacuo. The crude product was recrystallized from toluene/*n*-heptane to give Cu(dcp-DTSQ)$_2$.1.5H$_2$O as a dark brown crystalline material. Yield: 21.1 mg, 0.0325 mmol, 36%.

Positive ion FAB mass spectrum (*m/z*): 637 (18%), 623 (46, Cu(LH)$_2$ + 2H), 343 (100, Cu(LH$_2$)). Anal. Calcd for $C_{28}H_{41}CuN_4O_{1.5}S_4$: C, 51.78; H, 6.36; N, 8.63. Found: C, 52.00; H, 6.70; N, 8.60. IR (KBr, region from 1800 to 1500 cm^{-1}): 1706, 1629 cm^{-1}.

Pd(dcy-DTSQ)$_2$·2H$_2$O. To a solution of the ligand (209.5 mg, 0.679 mmol) in hot DMSO (15 mL) was added a solution of $Pd(OAc)_2$ (77.3 mg, 0.344 mmol) in hot DMSO (6 mL). A dark brown solution resulted immediately, and a dark green precipitate deposited upon cooling. This precipitate was collected and dried in vacuo. Recrystallization from either dichloromethane/acetonitrile or dichloromethane/methanol gave Pd(dcy-DTSQ)$_2$·2H$_2$O as dark green crystals. Yield: 115 mg, 0.152 mmol, 45%.

Positive ion FAB mass spectrum (*m/z*): 721 (100%, M(LH)$_2$ + H). Anal. Calcd for $C_{32}H_{50}N_4O_2PdS_4$: C, 50.75; H, 6.65; N, 7.40. Found: C, 50.80; H, 7.00; N, 7.28. ^{13}C NMR (chloroform-*d* with a small amount of methanol-d_4 added): δ 24.15, 25.17, 34.03, 55.15, 157.76 (C=N), 192.8 (C=S). UV–vis (chloroform): λ_{max} (log ϵ) = 458 (4.21), 364 (shoulder), 344 (shoulder), 314 (shoulder), 294 (4.69) nm. IR (KBr, region from 1800 to 1500 cm^{-1}): 1712, 1637 cm^{-1}.

Pd(dcp-DTSQ)$_2$. To a solution of the ligand (61.4 mg, 0.219 mmol) in hot DMSO (3 mL) was added a solution of $Pd(OAc)_2$ (25.4 mg, 0.113 mmol) in hot DMSO (2 mL). A dark yellow-brown solution resulted immediately. After cooling to 25 °C and standing for 15 h, a predominantly dark green precipitate was collected, washed with DMSO, and dried in vacuo. Attempts to purify this crude Pd(dcp-DTSQ)$_2$ by recrystallization were unsuccessful. The dark green product could not be separated from a visible quantity of a brown impurity. Crude yield: 35.8 mg, 0.0510 mmol, 47%.

Positive ion FAB mass spectrum (*m/z*): 679 (40%), 665 (100, M(LH)$_2$ + H), 386 (49, M(LH$_2$)).

X-ray Data Collection, Reduction, Solution, and Refinement for Pd(dcy-DTSQ)$_2$·2H$_2$O. A green prism crystal of Pd(dcy-DTSQ)$_2$·2H$_2$O having approximate dimensions of 0.100 × 0.200 × 0.200 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Cu Kα radiation and a 12-kW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $69.14° < 2\theta < 69.85°$, corresponded to a monoclinic cell.

On the basis of systematic absences of $h0l$, $h \neq 2n$, and $0k0$, $k \neq 2n$, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/a$ (No. 14).

The data were collected using the ω–2θ scan technique to a maximum 2θ value of 112.5°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.42° with a take-off angle of 6.0°. Scans of $(0.94 \pm 0.30 \tan\theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 285.0 cm.

Of the 2625 reflections which were collected, 2467 were unique (R_{int} = 0.033). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

An empirical absorption correction, based on azimuthal scans of several reflections, was applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2076 observed reflections ($I > 3.00\sigma(I)$) and 267 variable parameters and converged (largest parameter shift was 1.92 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.030$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.044$.

The standard deviation of an observation of unit weight was 1.32. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and −0.46 e/Å^3, respectively.

Neutral-atom scattering factors were taken from Cromer and Waber.[22] Anomalous dispersion effects were included in F_c;[23] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[24] All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.[25] Positional parameters are given in Table I. Crystal data details are given in Table II.

Results

The *cis*-dithiosquaramide ligands dcy-DTSQ, dcp-DTSQ, and dbu-DTSQ were prepared from their respective squaramides by reaction with P_4S_{10} under conditions similar to those reported previously.[16,20b,21] The compounds were characterized by elemental analysis, electron-impact mass spectrometry, and, for dbu-

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(22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(23) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(25) TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp., 1985.

Table I. Positional Parameters and *B*(eq) Values (Å^2) for Pd(dcy-DTSQ)$_2$·2H$_2$O

atom	*x*	*y*	*z*	*B*(eq)
Pd(1)	$^1/_2$	$^1/_2$	$^1/_2$	2.67 (2)
S(1)	0.4730 (1)	0.63739 (6)	0.43170 (9)	3.39 (4)
S(2)	0.4288 (1)	0.53025 (6)	0.66445 (8)	3.27 (4)
O(1S)	0.7853 (4)	0.5948 (2)	0.7444 (3)	5.8 (2)
N(3)	0.3062 (3)	0.7297 (2)	0.7694 (3)	3.5 (1)
N(4)	0.3518 (3)	0.8325 (2)	0.5498 (3)	3.3 (1)
C(1)	0.4163 (4)	0.6772 (2)	0.5409 (3)	3.0 (1)
C(2)	0.3980 (4)	0.6332 (2)	0.6365 (3)	2.9 (1)
C(3)	0.3483 (4)	0.7074 (3)	0.6839 (3)	3.1 (1)
C(4)	0.3698 (4)	0.7550 (2)	0.5801 (3)	2.8 (1)
C(5)	0.3756 (4)	0.8716 (3)	0.4447 (4)	3.5 (2)
C(6)	0.2878 (5)	0.8330 (3)	0.3247 (4)	3.7 (2)
C(7)	0.3144 (6)	0.8776 (4)	0.2195 (5)	4.8 (2)
C(8)	0.4673 (6)	0.8784 (4)	0.2346 (5)	5.5 (2)
C(9)	0.5547 (6)	0.9165 (4)	0.3557 (5)	5.4 (3)
C(10)	0.5302 (5)	0.8722 (3)	0.4622 (4)	4.3 (2)
C(11)	0.3003 (5)	0.6666 (3)	0.8587 (4)	3.7 (2)
C(12)	0.4031 (6)	0.6867 (6)	0.9812 (5)	8.6 (4)
C(13)	0.3948 (8)	0.6252 (8)	1.0799 (7)	9.8 (5)
C(14)	0.2506 (7)	0.6199 (5)	1.0824 (5)	6.5 (3)
C(15)	0.1479 (6)	0.5999 (6)	0.9621 (5)	7.5 (3)
C(16)	0.1572 (6)	0.6620 (5)	0.8645 (5)	7.0 (3)

Table II. X-ray Crystal Data for Pd(dcy-DTSQ)$_2$·2H$_2$O

$C_{32}H_{50}N_4O_2PdS_4$	fw = 757.42
a = 10.222 (3) Å	space group = $P2_1/a$ (No. 14)
b = 16.015 (3) Å	T = 21 ● 1 °C
c = 11.664 (1) Å	λ = 1.541 78 Å
β = 110.25 (1)°	ρ_{calcd} = 1.403 g/cm^3
V = 1791.4 (7) Å^3	$\mu_{Cu\ K\alpha}$ = 66.87 cm^{-1}
Z = 2	R = 0.030
transm factors: 0.79–1.00	R_w = 0.044

DTSQ, ^{1}H and ^{13}C NMR spectroscopy. A representative IR spectrum is shown in Figure 1, and a representative UV–vis spectrum is shown in Figure 2.

Neutral bis-ligand complexes of the general formula M(LH)$_2$·xH$_2$O were prepared by reaction of 2 equiv of ligand with 1 equiv of a divalent metal acetate in either DMF or DMSO solution. By this method complexes with Ni^{II}, Cu^{II}, and Pd^{II} were prepared. The complexes were characterized by elemental analysis and fast atom bombardment mass spectrometry. For each of the complexes, a mass ion envelope with maxima at (M(LH)$_2$ + H) or (M(LH)$_2$ + 2H) was observed by positive ion fast atom bombardment mass spectrometry. Occasionally ions of higher mass were observed, but they were less intense and, for the Ni^{II} and Pd^{II} derivatives, these higher mass ions were consistent with (M(LH)$_2$ + OH) or similar formulations involving water or hydroxide. For the Cu^{II} derivatives, the higher mass ions were consistent with (M$_2$(LH)$_2$ + 3H). For all of the complexes a fragment [M(LH) or M(LH$_2$)] corresponding to loss of one ligand from the parent was also seen. A representative IR spectrum is shown in Figure 1, and representative UV–vis spectra are shown in Figure 2. A diffraction study of the complex Pd(dcy-DTSQ)$_2$·2H$_2$O was undertaken, and the results are presented in Tables I and II and Figure 3.

Discussion

The complexation reaction between divalent transition metal acetates, M^{II} = Ni^{II}, Cu^{II}, and Pd^{II}, and *cis*-dithiosquaramide ligands occurs readily in DMF or DMSO to give intensely colored 2:1 species. The elemental analyses are consistent, in most instances, with the isolated products being hydrated, though the degree of hydration is variable. As is discussed below, Pd(dcy-DTSQ)$_2$ is obtained in crystalline form as a dihydrate, and both water molecules were located in well-ordered positions by X-ray diffraction.

^{1}H and ^{13}C NMR spectra for Ni(dbu-DTSQ)$_2$ and Pd(dcy-DTSQ)$_2$·2H$_2$O are consistent with their being diamagnetic species having symmetrically bound ligands. For example, the ^{13}C NMR spectrum of Ni(dbu-DTSQ)$_2$ shows six resonances which can be assigned in the following manner: four signals due to equivalent *n*-butyl groups (δ 13.51, 19.75, 32.57, and 46.59) and two signals due to symmetrically bound C$_4$N$_2$S$_2$ moieties (δ 159.17 and 193.23). Compared with unligated dbu-DTSQ, the resonance assigned to the C=N group of the cyclobutene ring has shifted upfield from δ 170.26 to 159.17. The resonance assigned to the thiocarbonyl carbons (δ 193.23) also undergoes an upfield shift as compared with the free ligand (δ 201.60). Such a change suggests that the SCCS group in the coordinated ligand is localized into a more dithiolene like form (S—C=C—S).[26] The ^{13}C NMR data for Pd(dcy-DTSQ)$_2$·2H$_2$O are in agreement with symmetrically bound ligands as evidenced by four resonances arising from two equivalent cyclohexyl groups (δ 24.15, 25.17, 34.03, and 55.15) and two resonances arising from symmetric and equivalent C$_4$N$_2$S$_2$ groups (C=N at δ 157.76 and C=S at δ 192.8). Owing to its poor solubility, no NMR data were obtained for the uncoordinated dcy-DTSQ ligand. Hard–soft acid–base (HSAB) considerations, the expected planarity of amide-like nitrogens, and the behavior of dithiooxamide[27] all suggest that the symmetrically found DTSQ ligands are coordinated in an S$_2$ rather than an N$_2$ fashion.

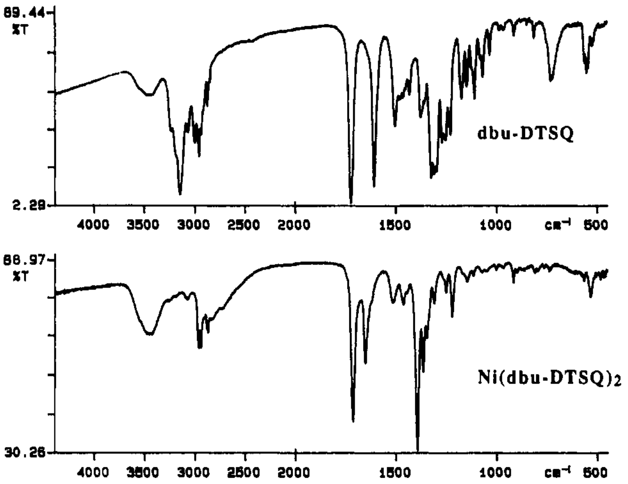

Figure 1. Infrared spectra for dbu-DTSQ and Ni(dbu-DTSQ)$_2$ dispersed in KBr.

Upon complexation significant changes are observed for some ligand vibrations. The free ligands each have a strong sharp band in the region from 1560 to 1610 cm^{-1} that generally shifts 35–70 cm^{-1} to higher energy upon complexation. For other squarate derivatives, bands in this range have been assigned as $\nu_{C=C}$;[28] however, for dithiosquaramides, assignment as $\nu_{C=N}$ seems more likely. Thus, the observed shift suggests that the NCCN half of the ligand adopts a structure more closely approximating

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(26) For comparison, the chemical shifts of the thiocarbonyl carbons in the dithiosquarate anion go from δ 220.5 to 188.6 upon methylation of both sulfurs. See: Seitz, G.; Mann, K.; Schmiedel, R.; Matusch, R. *Chem. Ber.* **1979**, *112*, 990.

(27) For example, several structurally characterized dithiooxamide complexes are known in which the ligands are bound in an S$_2$ fashion. Pd(*N*,*N'*-dicyclopentyldithiooxamide)$_2$: Hofmans, H. C.; Desseyn, H. O.; Dommisse, R. A.; van Nuffel, P.; Lenstra, A. T. H. *Transition Met. Chem.* **1984**, *9*, 213. [Cu(*N*,*N'*-dibenzyldithiooxamide)$_2$][ClO$_4$]$_2$: Antolini, L.; Fabretti, A. C.; Franchini, G.; Menabue, L.; Pellacani, G. C.; Desseyn, H. O.; Dommisse, R.; Hofmans, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 1921. [Ni(*N*,*N'*-diethyldithiooxamide)$_2$]Br$_2$: Ye, Q.-Y.; Busch, D. H. Unpublished results. A coordination mode other than S$_2$ is known for some dithiooxamide complexes of a single metal ion but only for tetradentate ligands. See: Ye, Q.-Y.; Nakano, Y.; Frauenhoff, G. R.; Whitcomb, D. R.; Takusagawa, F.; Busch, D. H. *Inorg. Chem.* **1991**, *30*, 1503.

(28) (a) Baglin, F. G.; Rose, C. H. *Spectrochim. Acta* **1970**, *26A*, 2293. (b) Skujins, S.; Webb, G. A. *Tetrahedron* **1969**, *25*, 3955.

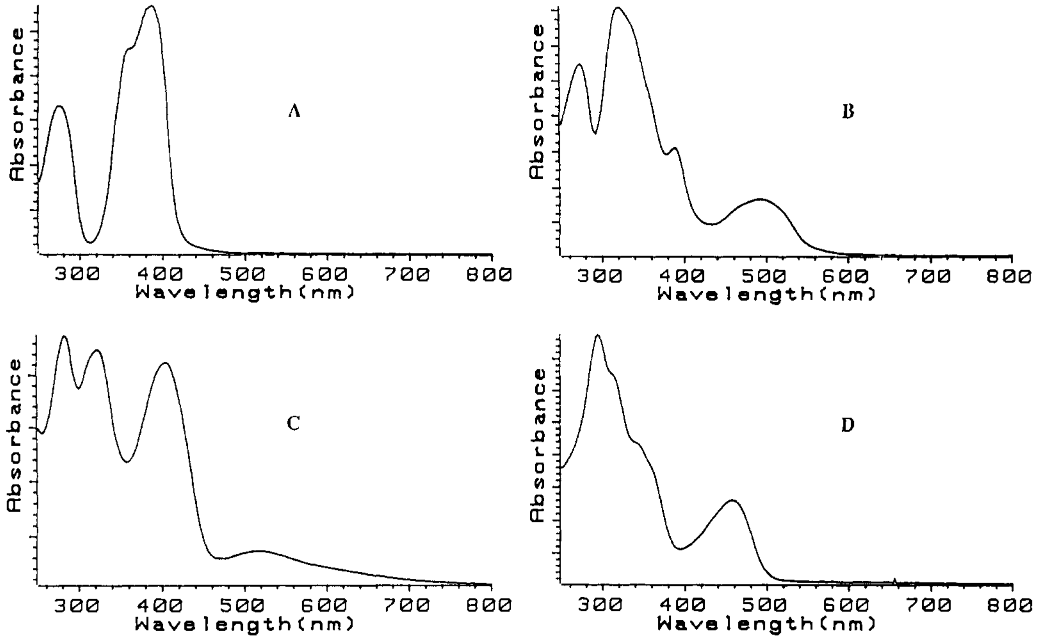


Figure 2. UV–vis spectra for dbu-DTSQ (A), Ni(dbu-DTSQ)$_2$ (B), Cu(dbu-DTSQ)$_2$·0.5H$_2$O (C), and Pd(dcy-DTSQ)$_2$·2H$_2$O (D) in chloroform solution. Absorbances are not to scale.

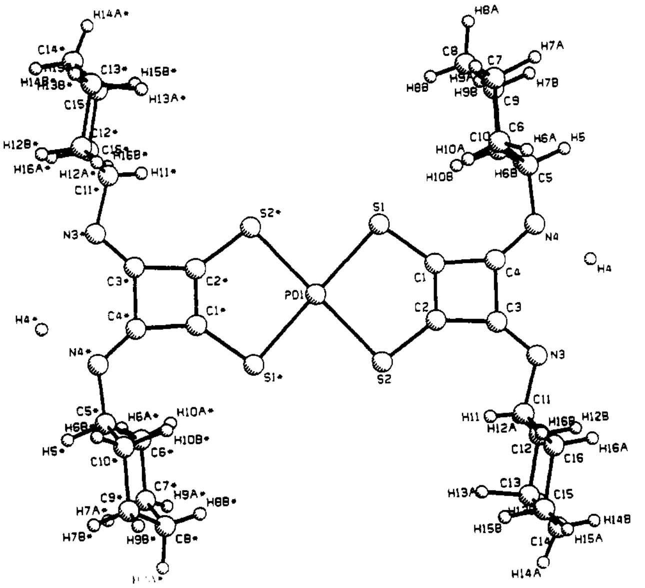
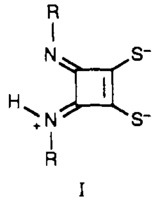


Figure 3. PLUTO drawing of Pd(dcy-DTSQ)$_2$·2H$_2$O. Water molecules are not shown.

an α-diimine (N=C—C=N).[29] Strong bands which appear in the region from 1200 to 1330 cm^{-1} in the free ligands also shift to higher energy upon coordination (approximately 60 cm^{-1}). However, owing to the complexity of the spectra in this region combined with the possible splitting of some bands, it was not possible to determine the absolute shift for any given band. For the tetrathiosquarate ligand, other workers have reported that bands in the region from 1200 to 1300 cm^{-1}, assigned as ν_{C-C-S}, undergo a shift to higher energy upon coordination.[14a] Interestingly, an intense sharp band seen near 1710 cm^{-1} in the free ligands is only slighty changed upon coordination. For squarate and dithiosquarate, bands in this region have been assigned as $\nu_{C=O}$. This obviously cannot be the assignment for DTSQ ligands. The 1710-cm^{-1} band may be a C$_4$ ring vibration, though if so it is at considerably higher energy than the C$_4$ ring vibration assigned for other derivatives of squaric acid (e.g. 1454 cm^{-1} for 3,4-bis(ethylthio)-3-cyclobutene-1,2-dione).[20b]

Electronic spectra for the complexes (Figure 2) show bands of substantial intensity in the visible region which are presumably of the charge-transfer type. For the Ni^{II} complexes a band is observed near 492 nm, and for Pd(dcy-DTSQ)$_2$·2H$_2$O a band is observed at 458 nm. Given that the complexes exhibit more bands in the region from 260 to 400 nm than can be accounted for by ligand–ligand transitions, other charge-transfer bands are indicated. The spectrum of Cu(dcy-DTSQ)$_2$·1.5H$_2$O in chloroform shows three poorly resolved absorptions at 386 (shoulder), 326, and 280 nm. Upon addition of a small amount of THF, the spectrum resolves considerably, exhibiting bands at 508 (broad), 396, 318, and 283 nm, and becomes very similar to the spectrum of Cu(dbu-DTSQ)$_2$·0.5H$_2$O (516, 404, 322, and 282 nm).

Crystals suitable for an X-ray diffraction study were grown for Pd(dcy-DTSQ)$_2$·2H$_2$O (**1**) from acetonitrile/dichloromethane. A PLUTO diagram of its molecular structure is shown in Figure 3. The molecule contains a square planar PdS$_4$ coordination environment with each ligand ligating in a didentate fashion through two sulfur atoms. The Pd–S distances, at 2.324 (1) and 2.3259 (9) Å, compare well with those observed for the bis(dithiosquarate) complex [Pd(C$_4$O$_2$S$_2$)$_2$]$^{2-}$ (2.333 (2) and 2.337 (2) Å for the tetraphenylphosphonium salt (**2**)[9b] and 2.345 (1) and 2.320 (1) Å for the potassium salt (**3**)[9a]). The S–Pd–S angle is rather large (92.96 (3)°) and consistent with a large bite angle for the



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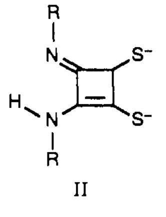

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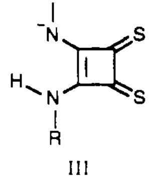
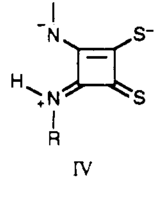


III



IV

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[29] For example, $\nu_{C=N}$ bands in α-diimines are usually found in the region from 1570 to 1660 cm^{-1}. Krumholz, P. In *Theory and Structure of Complex Compounds*; Jezowska-Trzebiatowska, B., Ed.; Pergamon Press: Oxford, U.K., 1964; p 217.

ligand. Similarly large S–Pd–S angles have been reported for **2** and **3** (92.9 (1) and 92.59 (2)°, respectively).

Coordination appears to cause the dithiosquaramide group to adopt a more localized bonding arrangement such as that depicted by resonance form I with at most minor contributions from the forms II–IV. Though none of the specific ligands in our study has been structurally characterized, the one *cis*-dithiosquaramide which has, *cis*-dipyrrolidino-C_4S_2 (**4**), shows significant delocalization in the C_4 ring as evidenced by roughly equivalent C–C distances (C(1)–C(2) = 1.452 (5) Å, C(1)–C(4) = C(2)–C(3) = 1.460 (5) Å, C(3)–C(4) = 1.473 (5) Å).[30] In contrast, for **1** the C(1)–C(2) bond is considerably shorter (1.386 (5) Å) and the C(3)–C(4) bond longer (1.510 (5) Å). The C(1)–C(4) and C(2)–C(3) bonds, at 1.461 (5) and 1.473 (5) Å, are nearly the same in **1**. Shorter C–N bonds (1.267 (5) and 1.287 (5) Å) and longer C–S bonds (1.689 (4) and 1.696 (4) Å) for **1** compared with **4** (C–N = 1.313 (4) and C–S = 1.645 (3) Å) are also consistent with a greater contribution from resonance form I. Despite the increased localization, the C–S distance is still shorter than a C–S single bond (ca. 1.82 Å).[31]

The hydrogen atom on N(4) was located, and the large N(3)–N(4) separation appears to preclude an intramolecular hydrogen bond. Two water molecules were located in the lattice in positions such that hydrogen bonding to the remaining acidic hydrogen of the coordinated ligand is likely. The hydrogen atoms of these water molecules were not found.

Acknowledgment. We thank Dr. Todd Williams of the University of Kansas for the mass spectral results and the 3M Co. for financial support.

Supplementary Material Available: For **1**, complete listings of bond lengths, bond angles, X-ray crystal data, conformation angles, intermolecular distances, general temperature factor expressions (*U*'s), and hydrogen atom coordinates (13 pages). Ordering information is given on any current masthead page.

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(30) Mattes, R.; Altmeppen, D.; Johann, G.; Schulte-Coerne, M.; Weber, H. *Monatsh. Chem.* **1982**, *113*, 191.

(31) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; p 108.