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Chelating Behavior of Quinazoline(1H,3H)-2,4-dithione

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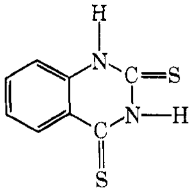
Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) complexes of quinazoline(1H,3H)-2,4-dithione are prepared. The structures of the complexes have been postulated on the basis of infrared, uv, and visible spectra and magnetic susceptibility data. The ligand field parameters are also calculated.

Quinazoline(1H,3H)-2,4-dithione (I) has two thiocarbonyl sulfur and two nitrogen atoms as potential donors.



I

It is obvious from the structure that all the four donor atoms cannot coordinate to the same metal ion simultaneously. If the two neighboring nitrogen and sulfur atoms coordinate to one metal ion and the other two coordinate to a different metal ion or ions, the structure of the complex formed should be polymeric. In case only two donor atoms per metal ion coordinate, the structure could be polymeric or monomeric and, therefore, it is of interest to investigate the nature of the complexes formed from the ligand. Pursuant to our interest[1-4] in the complexing properties of the ligands containing H—N—C(═S)– groups, this paper is to report the chelating behavior of I with divalent cations Co(II), Ni(II), Cu(II), Cd(II), and Hg(II). The infrared, uv, and visible spectra and the magnetic moments of these complexes have been examined in detail. Based on these studies, the structures of the complexes have been proposed.

Experimental Section

Preparation of Quinazoline(1H,3H)-2,4-dithione.—Quinazoline(1H,3H)-2,4-dithione, $C_8H_6N_2S_2$ (hereafter referred to as QH), was prepared by the method of Taylor, *et al.*[5] The ligand was recrystallized from 1-butanol before use. The compound analyzed correctly for $C_8H_6N_2S_2$. *Anal.* Calcd for $C_8H_6N_2S_2$: C, 49.5; H, 3.09; N, 14.5. Found: C, 49.2; H, 2.8; N, 14.3.

Preparation of Metal Complexes. (a) **Tris(quinazoline-(1H,3H)-2,4-dithionato)dicopper(II).**—A 0.8-g (~3 mmol) sample of $CuSO_4 \cdot 5H_2O$ was dissolved in ~20 ml of water and an excess of pyridine was added to it. A deep blue solution of Cu-py complex was thus formed. This solution was added to a hot solution of 1.2 g (~6 mmol) of ligand (I) in 10 ml of pyridine. A reddish brown precipitate of the complex $Cu_2(C_8H_4N_2S_2)Q_2$ was obtained. This was filtered out, then washed several times with pyridine, distilled water, alcohol, and ether successively. It was dried under suction and analyzed. *Anal.* Calcd for $Cu(C_8H_4N_2S_2)_2Q_2$: C, 40.8; H, 1.9; N, 11.9; Cu, 18.0. Found: C, 40.2; H, 1.5; N, 11.9; Cu, 17.5.

(b) **Ni(II) and Co(II) Complexes.** (i) **Bis(quinazoline-(1H,3H)-2,4-dithionato)dipyridinonickel(II).**—A 0.6-g (~3-mmol) sample of the ligand (I) was dissolved in about 10–15 ml of pyridine and 0.4 g (~1.5 mmol) of $NiCl_2 \cdot 6H_2O$ was dissolved in distilled water and a few milliliters of pyridine was added to it whereupon the color of the solution changed from green to blue. The two solutions were then mixed together and heated to reflux for about 30 min. The precipitated complex was filtered and washed successively with pyridine, distilled water, ethanol, and ether. It was dried in an oven at 60° overnight, yielding a greenish yellow complex. *Anal.* Calcd for $NiQ_2(py)_2$: C, 51.8; H, 3.3; N, 13.95; Ni, 9.9. Found: C, 52.2; H, 3.7; N, 13.3; Ni, 10.1.

(ii) **Bis(quinazoline(1H,3H)-2,4-dithionato)dipyridinocobalt-(II).**—$Co(NO_3)_2 \cdot 6H_2O$ 0.5 g (~1.6 mmole) was dissolved in distilled water and an excess of pyridine was added to the solution. This solution was then mixed with a pyridine solution of the ligand (I) prepared by dissolving 0.6 g of I in ~15 ml of pyridine. The mixture was then heated to reflux for ~30 min, and the precipitated complex was filtered out, washed with water, pyridine, ethanol, and ether, and dried in an oven at 110° for 6 hr, yielding an orange-yellow complex. *Anal.* Calcd for $CoQ_2(py)_2$: C, 51.8; H, 3.3; N, 13.95; Co, 9.9. Found: C, 52.2; H, 3.6; N, 13.98; Co, 9.8.

(iii) **Bis(quinazoline(1H,3H)-2,4-dithionato)cobalt(II).**—This complex was prepared by refluxing ~200 ml of a mixture of a solution of 0.6 g (~3 mmol) of the ligand (I) in 150 ml of boiling 1-butanol and a solution of 0.45 g (1.5 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ in ~50 ml of 1-butanol for 4 hr. On concentrating to nearly half the volume of the refluxed solution a reddish brown precipitate of the complex CoQ_2 separated out. It was filtered out and washed with boiling 1-butanol, ethanol, and finally with ether. It was dried at 120° for several hours. The analysis of the brown powder gave the following results. *Anal.* Calcd for CoQ_2: C, 43.1; H, 2.3; N, 12.6; Co, 13.5. Found: C, 43.5; H, 2.6; N, 12.4; Co, 12.9.

(iv) **Bis(quinazoline(1H,3H)-2,4-dithionato)nickel(II).**—This was prepared exactly in the manner of CoQ_2. About 0.6 g (~3 mmol) of ligand (I) was dissolved in ~150 ml of boiling 1-butanol and 0.4 g (~1.5 mmol) of $NiCl_2 \cdot 6H_2O$ was dissolved in ~50 ml of 1-butanol. The two solutions were filtered, mixed, and then refluxed for about 4 hr. The rest of the procedure was the same as in (iii). The brownish black complex NiQ_2 was dried at ~120° in an oven for 6–8 hr. *Anal.* Calcd for NiQ_2: C, 43.2; H, 2.3; N, 12.6; Ni, 13.5. Found: C, 43.1; H, 2.6; N, 12.5; Ni, 13.1.

The complexes CoQ_2 and NiQ_2 were also prepared by heating the corresponding pyridino complexes $CoQ_2(py)_2$ and $NiQ_2(py)_2$ at ~140–150° for several hours until no further loss in weight took place on heating.

(c) **Bis(quinazoline(1H,3H)-2,4-dithionato)cadmium(II).**—A 0.46-g (1.5-mmol) sample of $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in ~40 ml water. A clear solution of 0.6 g (3 mmol) of the ligand (I) was prepared in ~20 ml of pyridine. The two solutions were heated separately and the hot solutions were mixed in a beaker

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(1) U. Agarwala, S. K. Dikshit, and V. A. Narayan, *Can. J. Chem.*, **45**, 1057 (1967).

(2) U. Agarwala and S. K. Dikshit, *J. Inorg. Nucl. Chem.*, **30**, 1245 (1968).

(3) U. Agarwala and B. Singh, *ibid.*, **31**, 2515 (1969).

(4) U. Agarwala and B. Singh, *Indian J. Appl. Chem.*, in press.

(5) E. C. Taylor, A. McKillop, and R. N. Warrener, *Tetrahedron*, **23**, 891 (1967).

and stirred thoroughly. A yellow cadmium complex thus precipitated out which was filtered and washed with pyridine, water, ethanol, and ether. The complex was dried under suction. *Anal.* Calcd for CdQ_2: Cd, 22.5, C, 38.6; H, 2.0; N, 11.3. Found: Cd, 22.1; C, 38.1; H, 2.0; N, 11.9. Nitrate anion was found to be absent in the complex.

(d) **Bis(quinazoline(1H,3H)-2,4-dithionato)mercury(II).**—A solution of 0.4 g (~1.5 mmol) of $HgCl_2$ was prepared in 10 ml of hot water. This hot aqueous solution of $HgCl_2$ was mixed with a hot solution of 0.6 g (~3 mmol) of ligand I in pyridine. The yellow mercury complex precipitated out. The rest of the procedure was same as in (c). *Anal.* Calcd for HgQ_2: Hg, 33.9; C, 32.8; H, 1.7; N, 9.5. Found: Hg, 33.7; chloride ion, 0; C, 32.4; H, 1.6; N, 9.3.

Analyses.—The analyses of the metal ions were carried out by the standard methods.[6-8] Carbon, hydrogen, and nitrogen analyses were performed by the microanalytical section of the Indian Institute of Technology, Kanpur, India. The analytical results are given in the text.

Infrared Spectra.—Infrared spectra of the ligand and the complexes were recorded with a Perkin-Elmer Model 521 diffraction grating infrared spectrophotometer in the range of 4000–250 cm^{-1}. Samples were prepared as KBr disks. The results are given in Table I.

Table I

Assignments of the Major Infrared Bands of the Ligand and Complexes (cm^{-1})

Ligand	Complexes	Assignments
...	3400 m	Weak band characteristic of pyridine[a]
3235 m	...	ν_{asym}(N—H)
...	3200 m	ν(N—H) in complexes
3150 m	...	ν_{sym}(N—H)
1555 b, s	...	Thioamide band I[b]
...	1460 ± 10 s	Thioamide band I[b] in complexes
1325 s	1350 ± 10 m	Thioamide band II[c]
1290 m	1260 ± 10 m	Thioamide band II[c]
...	1080 m	Characteristic of pyridine ring[a]
...	1060 ± 5 m	ν(C—N) or mixed band due to ν(C—N) + a little ν(C=S)
1040 m	...	Thioamide band III[d]
...	1000 m	Thioamide band III in the complexes[d]
...	890 m	Thioamide band IV in the complexes[e]
790	...	Thioamide band IV in the ligand[e]
760 m	760 m	C—H out-of-plane vibration
745 m	...	N—H out-of-plane vibration
730 m	...	N—H out-of-plane vibration
...	700 ± 10 m	N—H out-of-plane vibration in the complexes
...	680 ± 10	Thioamide band IV in the complexes
...	510 w	γ(M—N)[f]
...	340 w	ν(M—S)[g]

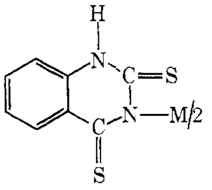
[a] These perturbations are found only in the complexes containing pyridine. [b] Due to ν(N—H) + ν(C—N). [c] Due to δ(N—H) + ν(C—N) + δ(C—H). [d] Mainly due to ν(C=S) and ν(C—N). [e] Mainly due to ν(C=S); the position of this band varies by ±20 cm^{-1} with a minimum in the Hg complex (870 cm^{-1}) and a maximum in the cobalt complex (910 cm^{-1}). [f] The position of this band varies with the metal by ±15 cm^{-1} with a maximum in the cadmium complex (520 cm^{-1}) and a minimum in the cobalt complex (505 ± 15 cm^{-1}). [g] The position of this band varies with the metal ion by ±20 cm^{-1} having a maximum value in mercury and copper (360 cm^{-1}) and a minimum value in nickel and cadmium (320 cm^{-1}).

Magnetic Susceptibility Measurements.—The magnetic susceptibilities of these complexes were determined with the help of a Gouy balance. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard and the diamagnetic corrections were estimated by a method outlined by Figgis and Lewis.[9] The results are given in Table II.

Uv and Visible Spectra.—Reflectance spectra of the metal complexes and the ligand were recorded on a Beckman DU spectrophotometer using the standard Beckman reflectance attachment and magnesium oxide as reference. The absorption of the cobalt complex was also recorded on a Cary 14 recording spectrophotometer in Nujol mull between 650 and 1500 mμ. The results are given in Table II.

Results and Discussion

The analytical data of the complexes show that except for the copper complex they are generally of two types: MQ_2 (M = Cd(II), Hg(II), Co(II), and Ni(II)) and $MQ_2(py)_2$ (M = Co(II) and Ni(II)). The stoichiometry of the copper complex is Cu_2Q_3. No other anions or cations except the ligand molecules have been detected in the complexes. Comparing these stoichiometries with the known preference of all of the metal ions for a coordination of four or six, it would appear rather certain that in all of the complexes except the copper complex, the ligand functions as a bidentate one. In the case of copper, however, the ligand appears to be tridentate. When the ligand is behaving as a bidentate, the metal ions can form either a simple salt (II) by linking with one of the nitrogen atoms or an inner complex (III) or a polymer (IV) by forming bonds with nitrogen and sulfur. (The ligand (I) as described by Taylor, *et al.*, exists as a dithione in the free state, but the probability of tautomerism in the thiol form[10] during the reaction cannot be overlooked, in which case complexes are formed by replacing the proton of the thiol group with the metal ion. However, the thione form of the ligand has been used here whereby a coordinate bond is formed by donating a lone-pair electron of the thiocarbonyl sulfur to the metal atom.) (In the accompanying structures, the coordination utilizing 2,3 positions has been shown, however, the coordination utilizing 1,2 or 3,4 positions may also take place.)



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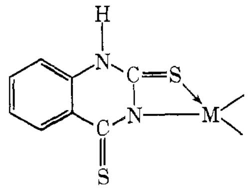
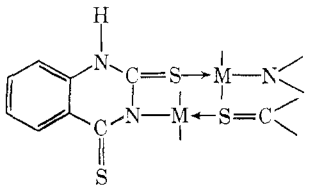


III



IV

No systematic study of the vibrational spectra of the ligand has been made. Thus, the infrared spectra of

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(6) A. I. Vogel, "A Textbook of Quantitative Inorganic Chemistry," Longmans, Green and Co., London, 1962, pp 358, 377, 389, 527, 528.

(7) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1958, pp 77, 199.

(8) I. Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Co., Philadelphia, Pa., 1941, p 455.

(9) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

(10) H. L. Yale, *J. Am. Chem. Soc.*, **75**, 675 (1953).

TABLE II

MAGNETIC MOMENTS, BANDS OF THE ELECTRONIC SPECTRA OF THE COMPLEXES, AND THEIR ASSIGNMENTS

Complexes	Magnetic moments μ_{eff}, BM	Position of the absorption band, mμ (cm^{-1})	Rel max	Assignments
$NiQ_2(py)_2$	3.40	1060 (9524)	8	$^3A_{2g} \rightarrow {}^3T_{2g}$
		900 (11,110)	6	$^3A_{2g} \rightarrow {}^3T_{2g}$
		620 (16,130)	7	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
		450 (22,220)	19	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
NiQ_2	3.23	1110 (9010)	4	$^3B_{1g} \rightarrow {}^3E^a{}_g$
		900 (11,110)	4	$^3B_{1g} \rightarrow {}^3B_{2g}$
		665 (15,040)	22	$^3B_{1g} \rightarrow {}^3A_{2g}$
		600 (16,670)	26	$^3B_{1g} \rightarrow {}^3F^b{}_g$
		450 (22,220)	38	$^3B_{1g} \rightarrow {}^3T_{1g}(P)$
$CoQ_2(py)_2$	4.24	1300 (7700)	6	$^4T_{1g} \rightarrow {}^4T_{2g}$
		650 (15,400)	31	$^4T_{1g} \rightarrow {}^4A_{2g}$
		540 (18,520)	40	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
CoQ_2	3.15	975 (10,260)	36	. . .
		712 (14,550)	25	. . .
		600 (16,670)	32	. . .
		525 (19,050)	37	. . .
$Cu_2(C_8H_4N_2S_2)Q_2$	Diamagnetic	675 (14,814)	0.5	$d_{xy} \rightarrow d_{x^2-y^2}$
		712 (14,550)	1.0	$d_{yx} \rightarrow d_{z^2}$
		950 (10,530) (unsym)	16	$d_{xy} \rightarrow d_{xz}$
				$d_{xy} \rightarrow d_{yz}$
CdQ_2 and HgQ_2	Diamagnetic	. . .		. . .

the ligand and the metal complexes were examined for assignment of the major bands of the ligands and to establish the structure of the complexes. The main infrared absorption frequencies of the ligand and the complexes with their band assignments are given in Table I. Since coordination was believed to take place through nitrogen and thiocarbonyl sulfur atoms, the major shifts are expected to be in the positions of the bands arising owing to the stretching of bonds and bending of angles with two HNCS groups of the ligand. Such major shifts in the spectra along with the discussion are summarized below.

(a) Two strong, although not very sharp, bands present around 3235 and 3150 cm^{-1} in the ligand, which have been assigned[11] to ν_{asym}(N-H) and ν_{sym}(N-H) modes of vibration, respectively, disappeared in the spectra of the complexes and a new band appeared around 3200 cm^{-1} (the broadening of these bands may be due to intermolecular interaction). This could most probably be explained on the assumption that during the formation of the complexes, one of the N-H groups of ligand I is deprotonated with the formation of a metal to nitrogen bond. In such a situation one should expect the absence of any intramolecular interaction between the N-H stretching modes and thereby one single band due to ν(N-H) should appear in the spectra of the complexes.

(b) Owing to close proximity of two thioamide (H—N—C(=S)–) groups in the ligand it would be rather certain that its four characteristic bands[12,13] will either be broad or split ones due to the strong interaction between the vibrational modes of the two groups.[14] The frequencies corresponding to these bands are given in Table I. These bands disappear in the spectra of the complexes and the new bands around 1460, 1060, 1000, 890, and 680 cm^{-1} appear indicating that the interaction between two thioamide groups in the complexes is different from that of those in the ligand. Assuming the deprotonation of one of the N-H groups as mentioned in the foregoing paragraph and coordination of the metal ion with sulfur, the following assignments to the new bands in the complexes could be made. The new band around 1460 cm^{-1} may be the thioamide band (I), which has been shifted from its original position (1555 cm^{-1}). The two bands around 1060 and 1000 cm^{-1} possibly arise owing to the splitting of the band at 1040 cm^{-1} which is mainly due to the mixing[12,13] of ν(C=S) and ν(C—N). Similarly, it appears that the thioamide band (IV) at 790 cm^{-1} in the ligand which is mainly due to ν(C=S)[15] splits into two new bands appearing around 890 and 680 cm^{-1}. The shifting of the thioamide band (IV) shows that most probably the bonding between the metal and thiocarbonyl sulfur is present in the complexes. It is also suggested that the band around 680 cm^{-1} contains the major contribution of the ν(C=S) which is coordinated to the metal ions while the band around 890 cm^{-1} contains the major contribution of the uncoordinated ν(C=S) mode.

(c) There are two bands appearing at 730 and 745 cm^{-1} in the spectrum of the ligand. These have been assigned to symmetric and antisymmetric N-H out-of-plane bending. In the complexes the band at 745 cm^{-1} disappears while the band at 730 cm^{-1} shifts to a band at a lower frequency (~700 cm^{-1}). The disappearance of one of these two bands and the red shift of the other band supports the assumption that one of the N-H bonds in the complexes is deprotonated. The band at 700 cm^{-1} in the spectra of the complexes may

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[11] A. Albert and E. Spinner, *J. Chem. Soc.*, 1221, 1237 (1960).

[12] C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).

[13] C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

[14] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

[15] I. Suzuki, *Bull. Chem. Soc. Japan*, **35**, 1286, 1449, 1456 (1962).

thus be assigned to the remaining N–H out-of-plane bending mode of vibration.

(d) Most of the characteristic bands of pyridine in nickel and cobalt complexes shift after complexation to lower frequencies by ~ 20 cm^{-1} indicating interaction of pyridine in the pyridine containing complexes $CoQ_2(py)_2$ and $NiQ_2(py)_2$.

(e) In the region 250–650 cm^{-1}, two new but somewhat broad bands appear in the spectra of the complexes. The new bands around 340 and 510 cm^{-1} are assigned to ν(M–S)[16] and ν(M–N)[17] modes of vibration, respectively.

(f) The absence of the weak band in the region of 2600 cm^{-1} in the spectra of the ligand and those of the complexes suggest that the ligand and the complexes are present in thione and not in thiol form.

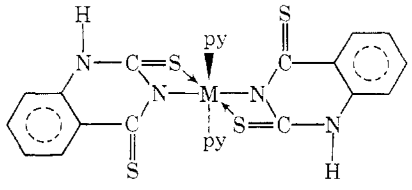
The preceding discussion of the infrared spectra of the complexes indicates (i) that the ligand is acting as bidentate except in copper complex and (ii) that the bondings with the metal ions in the complexes are through thiocarbonyl sulfur and nitrogen of the deprotonated N–H group, thus forming an inner complex type of structure (III) and not the salt type of structure (II). It is hard to distinguish between the inner complex structure (III) and polymeric structure (IV). However, the polymeric structure (IV) is preferred over structure III owing to complete insolubility in most of the common organic or inorganic solvents. The brownish black CoQ_2 and NiQ_2 dissolve in pyridine to form an orange-yellow $CoQ_2(py)_2$ complex and a greenish yellow $NiQ_2(py)_2$ complex which give the identical infrared spectra and the analyses as those of the same respective complexes prepared by methods (i) and (ii) under heading (c).

Visible Spectra and Magnetic Properties.—The magnetic and spectral properties of the complexes were studied to understand the spatial arrangements of the ligand around the metal ions. The magnetic moment corrected for ligand diamagnetism, the positions of the electronic absorption bands, and their most probable assignments are given in Table II.

The observed values of the effective magnetic moments of the nickel(II) complexes $NiQ_2(py)_2$ and NiQ_2 are 3.40 and 3.23 BM, respectively. These values are similar to those reported[18–20] for the octahedral or distorted octahedral complexes.

The reflectance spectrum of the $NiQ_2(py)_2$ complex shows three major absorption bands whose positions are characteristic of those found for octahedral complexes of bivalent nickel. This is taken as evidence in support of the octahedral arrangement of the ligand around the nickel ion in $NiQ_2(py)_2$. Besides these three bands, another weak, broad shoulder at 900 mμ is also present in this complex. This might arise owing to a slight departure[21] from the O_h symmetry toward D_{4h}. [There is a possibility[22] of this band arising from the $^3A_2(F) \rightarrow {}^1T_2(D)$ transition. However, the authors prefer that this band is due to the departure from O_h symmetry toward D_{4h} which is obvious from magnetic data also.] As such, under such a symmetry all the three bands would be expected to split up. The amount of splitting in first band ($^3A_{2g} \rightarrow {}^3T_{2g}$) may be taken as a measure ($^{35}/_{4}Dt$) of the degree of distortion.[23,24] The other two bands (*viz.*, 620 and 450 mμ) would also be expected to split to the extents of ($2Ds - {}^5/_4Dt$) and ($5Dt - 3Ds$), respectively. Any splitting which there may be in these bands is not resolved. However, the 620-mμ band is somewhat unsymmetrical on the low-frequency side. From the positions of these spectral bands, the values of Dq, B', and β were calculated to be 1110 cm^{-1}, 600 cm^{-1}, and 0.6, respectively. It may be noted that B' and β values for the complex are quite low. This puts the ligand quinazoline(1H,3H)-2,4-dithione toward the strong end of the nephelauxetic series. It was pointed out by Schaffer[25] and later on by Jørgensen[26] that the ligands which coordinate through sulfur atom frequently cause very pronounced nephelauxetic effects. It could, therefore, be said that the observation of large nephelauxetic effects in our complexes independently demonstrates that the metal atom is coordinated with ligand I through the sulfur atom.

The study of the reflectance spectrum of NiQ_2 shows a significant difference from the typical O_h type of complexes in that the bands in the 1000- and 600-mμ regions are split up into two peaks of each. This suggests the complex to be of lower symmetry than O_h, probably D_{4h}. Assuming the D_{4h} symmetry and the axial ligands to be weakly coordinated, the most probable assignments[27] of the absorption bands are given in the Table II. The values of $Dq^{(xy)}$ (1110 cm^{-1}), Dt (194 cm^{-1}), $Dq^{(z)}$ (720 cm^{-1}), and Ds (965 cm^{-1}) as calculated from the position of these bands are well within those found for other bivalent nickel complexes.[24] Thus, on the basis of ir and visible spectra and the magnetic moment values, structures V and VI are proposed for nickel complexes.



V[28]

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(23) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964).

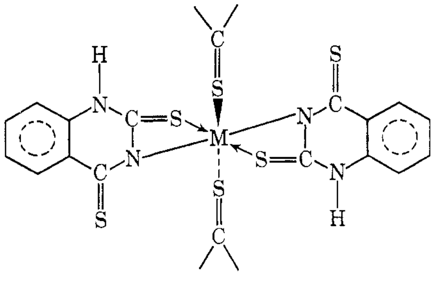
(24) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 2114 (1966).

(25) C. E. Schaffer, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 24N.

(26) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2017 (1962).

(27) R. A. Krause, C. Guy, and M. L. Hooker, *Inorg. Chem.*, **5**, 1825 (1966).

(28) The polymeric structure in which metal ion is coordinated to various molecules of the ligand cannot be ruled out.



VI[28]

The reflectance spectrum of the complex $CoQ_2(py)_2$ also shows three bands at 1300, 650, and 540 mμ. These positions are typical of octahedral cobalt complexes. Assuming the O_h symmetry around Co^{2+} ion, the assignments of these bands are given in Table II. Fitting the peaks[29] at 1300 and 540 mμ gives $Dq = 847\ cm^{-1}$, $B = 770\ cm^{-1}$, and $\beta = 0.69$ and places the two-electron $^4T_{2g}(F) \rightarrow {}^4A_{2g}(F)$ absorption band at 15,250 cm^{-1}. The observed band at 15,400 cm^{-1} corresponds very well with the calculated one.

The magnetic moment of the complex $CoQ_2(py)_2$ is 4.24 BM. This seems to be on the low side for the octahedral cobalt(II) complex. However, octahedral complexes having magnetic moments as low as 4.20 BM[30] are known. The possible postulated reason for the low value of the magnetic moment of the cobalt(II) complex may be the tetragonal distortion along the Z axis.[27] The structure of the complex $CoQ_2(py)_2$, thus, can be proposed similar to that given in V where M stands for the Co^{2+} ion.

The reflectance spectrum of CoQ_2 shows four weak bands at 975, 712, 600, and 525 mμ which presumably are d–d transitions. Although it is difficult to assign a definite structure for this complex on the basis of the positions of these bands alone, it appears that the field around the Co^{2+} ion has strong tetragonal character which manifests itself in the splitting of the orbitally degenerate terms, *viz.*, $^4T_{1g}$ and $^4T_{2g}$ in the octahedral symmetry. The evidence in support of the tetragonal character comes from the magnetic moment value 3.15 BM, a much too low value for an octahedral bivalent cobalt complex. (As discussed in the preceding paragraph, the low value might be due to the tetragonal distortion.[31]) Thus structure VI may also be assigned to the complex CoQ_2.

The stoichiometry of the copper complex $Cu_2(C_8H_4N_2S_2)Q_2$ is different from those of other metal ion complexes. A simple oxidation–reduction experiment shows the absence of copper in the monovalent oxidation state. Thus, in one-third of the ligand molecules both of the N–H groups ought to be deprotonated. Besides, this copper complex is diamagnetic. This is one of few copper(II) complexes[32–34] in which the spin paramagnetism normally associated with cupric ion is completely quenched ($\mu_{eff} = 0$) at room temperature in contrast to the partial quenching observed in many cupric complexes.[35] The diamagnetism indicates strong spin–spin interaction which might arise due to direct copper–copper linkage with the formation of either a δ bond by the overlap of $d_{x^2-y^2}$ orbitals[36,37] or a σ bond by the overlap of d_{z^2} orbitals.[38]

However, in quite a large number of cupric complexes, partial quenching of the paramagnetism is explained by the superexchange mechanism,[32] forming a σ or π bond. It is just possible that in the complex $Cu_2(C_8H_4N_2S_2)Q_2$, the spin–spin interaction might arise from both of these phenomena. It has been shown, however, that the known diamagnetic complexes[32–34] have a short copper to copper distance forming a direct metal–metal bond. Also it is generally seen that the superexchange phenomenon takes place[35] in those complexes where two copper atoms are linked through a monatomic bridge as in CuO. Taking this point into consideration, possibly a direct metal to metal bond appears to be a more plausible explanation for the quenching of the paramagnetism in the complex which might occur due to the presence of an easily polarizable sulfur atom, whereby a large transfer of electron density to the copper atoms takes place with the consequent increase in the overlap between the orbitals of different copper atoms.[33] It is not possible however, to prefer either a σ- or a π-bond formation in direct copper–copper interaction at this stage. The visible spectrum of the complex shows three weak bands at 675, 712, and 950 mμ. The last band is a broad and unsymmetrical one which can be resolved into two bands. In the D_{2h} symmetry of the field, the spectrum of the Cu^{2+} ion should show four d–d transitions[39] in the visible region. On the assumption of this symmetry, the assignments of the four bands given in Table II have been made on the basis given in ref 39. Tsuchida, *et al.*,[40,41] indicated that all of the copper complexes having metal to metal interaction absorb in the 375-mμ region. However, the location of this band in the copper complex is not possible owing to the presence of strong charge-transfer bands. Thus the insolubility in inorganic and organic solvents, stoichiometry, diamagnetism, and visible and infrared spectra indicate the structure VII for the copper complex. In this structure two of the three ligands are behaving as tridentate while one is bidentate.

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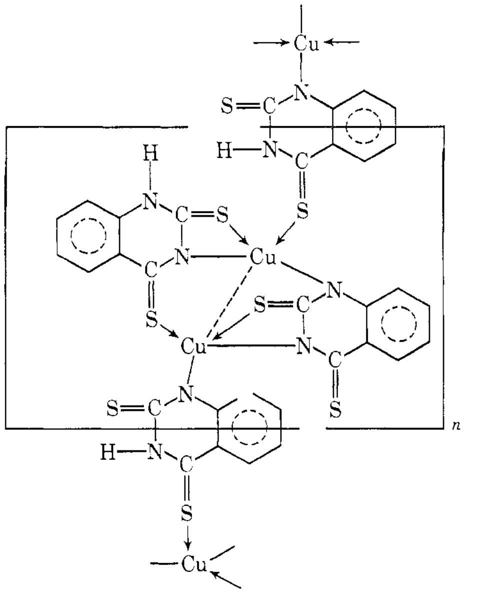

VII

Most of the Cd(II) and Hg(II) complexes mentioned in the literature are tetrahedral.[42] The complexes CdQ_2 and HgQ_2 are diamagnetic. Therefore, the tetrahedral arrangements of the ligand molecules around Cd(II) and Hg(II) are assigned to these complexes.

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Phosphorus-31–Phosphorus-31 Coupling in Metal Complexes Containing Two Different Phosphorus Ligands

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Phosphorus-31–phosphorus-31 coupling constants were determined from the ^{31}P resonance spectra of *trans*-Fe(CO)$_3$LL′, *cis* and *trans*-Mo(CO)$_4$LL′, and *cis*- and *trans*-Mo(CO)$_4$LL″ [L = $P(OCH_2)_3CR$, L′ = $P(N(CH_3)_2)_3$, and L″ = $P(OCH_3)_3$] whose syntheses are reported for the first time. These couplings are found to lie between those found for the analogous complexes in which both ligands are identical. Evidence is presented suggesting that the signs of the *cis* and *trans* complexes are negative and positive, respectively. The CO stretching frequencies in the mixed complexes are found in every case to lie between those of the analogous compounds wherein both ligands are the same.

Introduction

Few bis-monodentate phosphorus mixed-ligand complexes have been prepared[2] although a considerable number of such compounds have been synthesized wherein one of the ligands is a chelate.[3] Mixed-ligand complexes are useful in that quite precise values of ^{31}P–^{31}P couplings can be obtained directly from the ^{31}P spectrum since the phosphorus atoms are chemically nonequivalent. We report here the preparation of *trans*-Fe(CO)$_3$LL′, *cis*- and *trans*-Mo(CO)$_4$LL′, and *cis*- and *trans*-Mo(CO)$_4$LL″. Throughout this paper L = $P(OCH_2)_3CR$ [R = C_2H_5 or C_3H_7], L′ = $P(N(CH_3)_2)_3$, and L″ = $P(OCH_3)_3$. Comparison of the ^{31}P–^{31}P couplings for these systems with those wherein both ligands are the same[4] reveals the strong possibility that coupling in the *trans* complexes is positive whereas in the *cis* systems it is negative. The magnitude of the couplings appear to be consistent with the hybridization and effective nuclear charge changes expected upon varying the ligands.

Experimental Section

Infrared spectra were obtained in the specified solvents on a Perkin-Elmer Model 21 and Beckman IR 12 spectrometers. Proton nmr spectra were observed in 10–20% solutions in $CDCl_3$ on a Varian A-60 instrument using tetramethylsilane as an internal standard. Phosphorus-31 nmr spectra were observed in saturated solutions in $CDCl_3$ on a Varian HR-60 instrument using phosphoric acid as an external standard. Molecular weights were determined from mass spectra recorded on an Atlas CH-4 single-focusing spectrometer at an energy of 70 eV. Microanalyses were run by Galbraith Laboratories, Knoxville, Tenn.

cis- and *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(N(CH_3)_2)_3]$.—The monosubstituted complex $Mo(CO)_5[P(N(CH_3)_2)_3]$ was prepared as described by King.[5] A solution of methylcyclohexane (80 ml), $Mo(CO)_5[P(N(CH_3)_2)_3]$ (3.01 g, 7.5 mmol), and $P(OCH_2)_3C$-

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