# 569. *Metal Dithizone Complexes of Mercury and Cobalt.*

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The complex of dithizone formed with cobalt in the presence of air was found to contain three dithizone residues to one cobalt atom. Investigation of the stoicheiometry by direct titration and analysis, Job's method, magnetic moment, and infrared absorption shows that cobalt(III) is present. In the dithizone complexes of mercury, copper, and cobalt(III) there is very little hydrogen bonding in carbon tetrachloride solution.

While studying the use of dithizone as an analytical reagent Duncan and Thomas [1] found that cobalt was extracted into carbon tetrachloride with three dithizone residues per cobalt atom, in contrast to previously reported values of two.[2-4] It was also observed that the mercury and copper complexes with dithizone were more stable than was expected when compared with those of the other bivalent metals. This paper reports work on the structure and stabilities of these compounds.

## Experimental

*Purity of Reagents.*—Owing to the ease with which dithizone forms complexes with traces of many metal cations, solvents and reagents had to be carefully purified when used in more than traces. Carbon tetrachloride (" AnalaR ") was first shaken with concentrated sulphuric acid and then refluxed over and distilled from lime. Water, distilled once from alkaline 0·05% permanganate solution containing 0·1% of sodium hydroxide, was redistilled in all-Pyrex glass apparatus, and stored in a clean Jena-glass bottle fitted with Pyrex delivery tubes. The " AnalaR " acids gave negative tests with dithizone under experimental conditions. Before use, " AnalaR " nitric acid was boiled to remove nitrous acid.

Dithizone (diphenylthiocarbazone, $C_{13}H_{12}N_4S$, designated here as $H_2Dz$) was purified as described by Welcher,[5] but instead of the purified dithizone being isolated as a solid it was precipitated from ammoniacal solution with hydrochloric acid in the presence of carbon tetrachloride, in which it immediately dissolved. The resulting solution ($\sim 10^{-3}$M), which was stored under 1% aqueous sulphur dioxide in a cool darkened cupboard, was diluted as required. Dithizone solutions were standardized regularly with " AnalaR " lead or silver solutions.[6] Buffer solutions were treated before use with dithizone to remove interfering cations.

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[1] Duncan and Thomas, *J. Inorg. Nuclear Chem.*, 1957, **4**, 376.
[2] Fischer, *Angew. Chem.*, 1937, **50**, 919.
[3] Pilipenko, *Zhur. analit. Khim.*, 1953, **8**, 286.
[4] Miyakawa and Uemura, *Bull. Chem. Soc. Japan*, 1951, **24**, 25.
[5] Welcher, " Organic Analytical Reagents," Van Nostrand, New York, 1948, Vol. III, p. 466.
[6] Welcher, *op. cit.*, pp. 506, 519.

Cobaltous solutions were prepared from " AnalaR " cobalt sulphate heptahydrate (Found: Co, 21·05. Calc.: 20·97%[7]); copper solutions from " AnalaR " copper sulphate pentahydrate, and mercuric solutions by dissolving " AnalaR " mercuric oxide in " AnalaR " nitric acid.

*Radio-tracer Solutions.*—(i) $^{203}Hg(NO_3)_2$. Neutron-irradiated mercuric oxide (0·1081 g.; from A.E.R.E., Harwell) was dissolved in " AnalaR " nitric acid and diluted to 50 ml. This solution was then diluted 500-fold with dilute nitric acid to give a solution containing 4 μg. of $Hg^{2+}$ per ml. ($2 \times 10^{-5}$M) and M/10 with respect to nitric acid. (ii) $^{60}Co(NO_3)_2$. Irradiated cobalt metal (4·0$_0$ mg.) was dissolved in 0·5 ml. of " AnalaR " concentrated nitric acid and diluted to 100 ml. with water. The resulting solution had a pH of 2 and contained 40 μg. of cobalt per ml. ($6·8 \times 10^{-4}$M). By Feather's[8] and Bleuler and Zünti's[9] methods these two isotopes were found to be radiochemically pure.

*Storage.*—Solutions were stored in glassware treated with " Desicote " to prevent exchange of cations between the glass and the solution. Glass taps and joints were greased (where necessary) with B.D.H. rubber and paraffin lubricant. This grease was found to give a negligible reaction with dithizone (50 mg. of grease contained metal cations equivalent to <0·1 ml. of $10^{-5}$M-dithizone solution).

*Partition Coefficients.*—The partition coefficients of mercury and cobalt dithizone complexes between water and carbon tetrachloride ($P_{M(HDz)_n} = [M(HDz)_n]_{CCl_4}/[M(HDz)_n]_{H_2O}$) were determined by a method similar to that used by Geiger and Sandell[10] for the copper dithizone complex, except that a radiochemical instead of a spectroscopic method was used to estimate the concentrations of the complex in the two phases.

The partition coefficient of the mercury dithizone complex was determined by vigorously shaking 25 ml. of a carbon tetrachloride solution of dithizone ($0·98 \times 10^{-3}$M) for 60—75 min. in a 1-l. stoppered flask with 800 ml. of a solution containing excess of mercury [(1·68—2·50) $\times 10^{-5}$M)], labelled with $^{203}$Hg. The acidity and ionic strength of the solution were adjusted within the range 0·05—1·0M with hydrochloric acid and sodium chloride respectively. The two phases were carefully separated, and the activity of 5 ml. of the carbon tetrachloride phase was measured in a liquid Geiger–Müller counter, type D.M.6; 500 ml. of the aqueous phase were shaken with a further 5 ml. of carbon tetrachloride, and after separation the activity of the organic phase was measured as above. These determinations were carried out at 24° and 34·8°. The activities of the two carbon tetrachloride solutions were used for calculation of the partition coefficient of the mercury dithizone complex at the two temperatures. In the case of the cobalt dithizone complex the pH of the aqueous solution was varied between 5·54 and 7·81 by using sodium acetate–acetic acid and ammonia–ammonium chloride buffers. The determinations were carried out at 15·5°, 25·0°, and 34·8° with cobalt concentrations of (1·13—2·55) $\times 10^{-5}$M and a dithizone concentration of $0·93 \times 10^{-3}$M. The partition coefficient was determined as for the mercury dithizone complex.

*Equilibrium Constants.*—The equilibrium constants of the mercury and cobalt dithizone complexes, $K_{M(HDz)_n}$, were calculated from the variation of the distribution ratio, *q*, with acidity at constant added metal ion and dithizone concentrations, where

$$q = [\text{Total M}]_{CCl_4}/[\text{Total M}]_{H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In the case of the mercury dithizone complex, 15 ml. of a carbon tetrachloride solution of dithizone ($\sim 3 \times 10^{-5}$M) were shaken for 3 min. at 25° with 20 ml. of a mercury solution ($\sim 1 \times 10^{-5}$M), labelled with $^{203}$Hg, at various acidities (0·05—3·0M with respect to hydrochloric acid). Trial runs showed that equilibrium was established in less than 1 min. Samples (1 ml.) of each phase were evaporated to dryness and their activities were measured with an end-window Geiger–Müller tube. These activities were used to calculate values of *q* at the various acidities. As these samples were " weightless " no correction for the self-absorption of the weak β particles of $^{203}$Hg was necessary. For the cobalt dithizone complex the volumes of both phases were 15 ml. The aqueous phase was $\sim 1 \times 10^{-5}$M with respect to $Co^{2+}$, labelled with $^{60}$Co, and buffered with sodium acetate–acetic acid mixtures in the pH range 3·7—7·0. The total ionic concentration was kept in the range 0·005—0·15M, and the dithizone concentration in the range (2·9—4·2) $\times 10^{-5}$M. Trial runs showed that for a given set of conditions constant values of *q* were obtained after shaking for 2—5 min., depending on the pH. As a

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[7] Vogel, " Quantitative Inorganic Analysis," Longmans, Green & Co., London, 1948, p. 549.

[8] Feather, *Proc. Camb. Phil. Soc.*, 1938, **34**, 599.

[9] Bleuler and Zünti, *Helv. Phys. Acta*, 1946, **19**, 375.

routine the system was shaken for 12 min. at 25° and $q$ was determined from the activity of 0·5 ml. aliquot parts of each phase evaporated to dryness.

*Determination of the Cobalt to Dithizone Ratio in the Cobalt Dithizone Complex.*—Evidence on the stoicheiometry of this complex was obtained by use of the following procedures:

(i) *Analysis.* Several samples of the cobalt dithizone complex were prepared by shaking, for 45—60 min., 1 l. of a $10^{-3}$M-solution of dithizone in carbon tetrachloride with 250 ml. of a 4 × $10^{-3}$M-aqueous solution of cobalt sulphate, buffered to pH 6·7 with sodium acetate. The organic layer was separated and filtered, and the bulk of the solvent distilled off under reduced pressure (at 35—40°). The precipitated cobalt dithizone complex was filtered off from the liquor and dried at 50° under reduced pressure (5—10 mm.). (This complex is unstable in many solvents and also to mild heating. In the only solvent found suitable, carbon tetrachloride, its solubility relationships in the range 0—50° are unfavourable for recrystallisation.) Analyses for hydrogen, carbon, sulphur, and cobalt were performed by Dr. W. Zimmerman of the C.S.I.R.O. Micro-analytical Laboratory.

(ii) *Direct titration of cobalt with dithizone.* This was carried out as previously described.[1]

(iii) *Modified Job's method.* The modifications of Job's method for determining the ligand to cation ratio in complexes as given by (*a*) Pilipenko [3] and (*b*) Miyakawa and Uemura [4] were repeated. In method (*a*) the cobalt and dithizone solutions (both 5·58 × $10^{-5}$M) were mixed in varying proportions to give a total volume of 10 ml. The cobalt solution was adjusted to pH 6·9 with sodium acetate before the mixing. After 15 minutes' shaking, the two phases were allowed to separate, an aliquot part of the carbon tetrachloride layer, equal to half the original volume of dithizone, was taken and diluted to 5·0 ml. with carbon tetrachloride, and the optical density measured at 5100, 5500, and 6200 Å with a Hilger ultraviolet spectrophotometer. Method (*b*) was performed at pH 6·0 and 7·1 with a cobalt concentration of 2·69 × $10^{-5}$M and a dithizone concentration of 4·20 × $10^{-5}$M and at pH 6·9 with both cobalt and dithizone concentrations of 5·58 × $10^{-5}$M. The titration was followed at 6200 and 5100 Å. After addition of each aliquot part of cobalt solution, the mixture was shaken for 10—15 min.

(iv) *Variation of* q *with* pH *at constant dithizone concentration.* With an initial cobalt concentration of 1·12 × $10^{-5}$M, the dithizone concentration was held constant at the various values of pH by using a large excess of dithizone (15 ml. of 8·80 × $10^{-4}$M). The method described above for the determination of $q$ for the cobalt dithizone system was repeated at 25°, sodium acetate–acetic acid and acetic acid–hydrochloric acid mixtures being used to control the pH.

(v) *Variation of* q *with dithizone concentration at constant* pH. Method (iv) was repeated at 25° with the aqueous phase kept at pH 4·27 ± 0·02 by a sodium acetate–acetic acid buffer. The dithizone concentration was varied between 8·5 × $10^{-4}$ and 6·2 × $10^{-6}$M and the cobalt concentration was 1·12 × $10^{-5}$M.

(vi) *Magnetochemical evidence.* Solid cobalt dithizone complex (50·89 mg.) was suspended on the beam of a conventional magnetobalance, with a field strength of about 10,000 gauss, and the magnetic moment determined by comparison with "AnalaR" nickel chloride as standard. The value of the moment obtained was 0·10 ± 0·15 Bohr magneton.

(vi) *Infrared spectra of metal dithizone complexes.* The infrared absorption due to the N–H stretching frequency was examined in a single-beam, double-pass Perkin–Elmer Model 112 recording infrared spectrophotometer with a 1 cm. cell to contain a saturated solution of the dithizone complex in dry carbon tetrachloride. The two copper complexes of dithizone were prepared by Geiger and Sandell's method,[10] solutions adjusted to pH 7·0 (for CuDz) and to pH 2·0 [for $Cu(HDz)_2$] being used. The mercury complex was prepared by an analogous method with the aqueous solution adjusted to a pH of 1·0.

## RESULTS AND DISCUSSION

*Mercury Dithizone Complex.*—(i) *Partition coefficient.* A direct extractive titration of mercury with dithizone confirmed that in acid solution (>M/50) two dithizone molecules react with one mercuric ion to form the mercury dithizone complex. The partition coefficient of this complex is given by

$$P_{\mathrm{Hg(HDz)_2}} = \overline{[\mathrm{Hg(HDz)_2}]_1}/[\mathrm{Hg(HDz)_2}]_1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[10] Geiger and Sandell, *Analyt. Chim. Acta*, 1953, **8**, 197.

where the bar refers to the organic phase, and the subscript 1 refers to the first equilibration. After removal of the organic phase, the aqueous solution is again shaken with fresh solvent, and hence we have:

$$P_{\mathrm{Hg(HDz)_2}} = \left\{\frac{\overline{[\mathrm{Hg(HDz)_2}]}_1}{\overline{[\mathrm{Hg(HDz)_2}]}_2} - 1\right\}\frac{v_2}{\overline{v_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $v_2$ and $\overline{v_2}$ are the volumes of the aqueous and the organic phase, respectively, used in the second equilibration. Now $\overline{[\mathrm{Hg(HDz)_2}]}_1$ and $\overline{[\mathrm{Hg(HDz)_2}]}_2$, the concentrations of the mercury dithizone complex in the organic phases in the two equilibrations, are proportional to the specific activities of the respective organic layers, *i.e.*,

$$P_{\mathrm{Hg(HDz)_2}} = \left\{\frac{\text{Activity of 5 ml. of organic phase after 1st equil.}}{\text{Activity of 5 ml. of organic phase after 2nd equil.}} - 1\right\}\frac{v_2}{\overline{v_2}} \quad . \quad (4)$$

where $v_2 = 500$ ml. and $\overline{v_2} = 5$ ml. for our conditions.

TABLE 1. *Partition coefficients of mercury dithizone complex between water and carbon tetrachloride.*

| $T$ | $[\mathrm{H^+}]$ (M) | Ionic strength | Initial $[\mathrm{Hg^{2+}}]$ (M × $10^5$) | Activity of 5 ml. of organic phase (counts/min.) 1st extraction | 2nd extraction | $P_{\mathrm{Hg(HDz)_2}}$ (× $10^{-3}$) |
|---|---|---|---|---|---|---|
| 24·0° | 1·0 | 1·0 | 1·88 | 3328 ± 26 * | 93·1 ± 5·0 | 3·47 |
| 24·0 | 0·1 | 1·0 | 1·68 | 4005 ± 30 | 105·0 ± 5·9 | 3·71 |
| 24·0 | 0·05 | 1·0 | 1·68 | 3984 ± 30 | 106·3 ± 5·9 | 3·64 |
| 24·0 | 0·5 | 0·5 | 1·88 | 3480 ± 28 | 95·0 ± 7·9 | 3·56 |
| 23·9 | 0·5 | 0·5 | 2·50 | 2273 ± 26 | 63·5 ± 4·6 | 3·48 |
| 23·9 | 0·05 | 0·1 | 1·88 | 3397 ± 27 | 94·2 ± 5·1 | 3·51 |
| 34·8 | 0·5 | 1·0 | 2·50 | 2016 ± 41 | 51·3 ± 4·0 | 3·83 |
| 34·8 | 0·1 | 0·5 | 1·88 | 3357 ± 26 | 90·2 ± 4·9 | 3·62 |

* All limits quoted in this paper are standard deviations.

The values of $P_{\mathrm{Hg(HDz)_2}}$ calculated by using this equation are given in Table 1, from which the mean value $P_{\mathrm{Hg(HDz)_2}}$ at 24·0° ± 0·1° is $3{\cdot}56 \times 10^3$ with a standard deviation of $0{\cdot}05 \times 10^3$. The mean of two determinations of $P_{\mathrm{Hg(HDz)_2}}$ at 34·8° was $3{\cdot}73 \times 10^3$, but it is doubtful if the difference from the value at 24° is significant.

(ii) *Stability constant.* A typical curve showing the variation of the percentage extraction of mercury by the organic phase, with the acidity of the aqueous phase is given in Fig. 1(*A*). As these extractions were performed from aqueous solutions containing chloride ion, the following equilibria must be considered:

$$\{\mathrm{HgCl}_n\}^{(2-n)+} \rightleftharpoons \{\mathrm{HgCl}_{(n-1)}\}^{(3-n)+} + \mathrm{Cl^-}$$

where $n = 1, 2, 3,$ or $4$.

$$\overline{\mathrm{H_2Dz}} \overset{P_a}{\rightleftharpoons} \mathrm{H_2Dz} \overset{K_a}{\rightleftharpoons} \mathrm{HDz^-} + \mathrm{H^+}$$

$$\mathrm{Hg^{2+}} + 2\mathrm{HDz^-} \overset{K_{\mathrm{Hg(HDz)_2}}}{\rightleftharpoons} \mathrm{Hg(HDz)_2} \overset{P_{\mathrm{Hg(HDz)_2}}}{\rightleftharpoons} \overline{\mathrm{Hg(HDz)_2}}$$

Since $[\mathrm{Hg(HDz)_2}]$ is negligible the total concentration of mercury in the aqueous phase, $C_{\mathrm{Hg}}$, is given by:

$$C_{\mathrm{Hg}} = [\mathrm{Hg^{2+}}]\left\{\sum_0^n K_n[\mathrm{Cl^-}]^n\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{where } K_n = [\{\mathrm{HgCl}_n\}^{(2-n)+}]/[\mathrm{Hg^{2+}}][\mathrm{Cl^-}]^n$$

$$\text{Now } K_{\mathrm{Hg(HDz)_2}} = [\mathrm{Hg(HDz)_2}]/[\mathrm{Hg^{2+}}][\mathrm{HDz^-}]^2 \quad . \quad . \quad . \quad . \quad . (6)$$

$$= \frac{\overline{[\mathrm{Hg(HDz)_2}]}[\mathrm{H^+}]^2\left\{\sum_0^4 K_n[\mathrm{Cl^-}]^n\right\}P_a{}^2}{\overline{[\mathrm{H_2Dz}]}^2 C_{\mathrm{Hg}} P_{\mathrm{Hg(HDz)_2}} K_a{}^2} \quad . \quad . \quad . \quad (7)$$

where $P_a = \overline{[H_2Dz]}/[H_2Dz]$ and $K_a = [H^+][HDz^-]/[H_2Dz]$ are the partition coefficient and the acidity constant of dithizone, respectively. Using equation (7), the values of $K_n$ given by Lindgren *et al.*[11] and the data of Fig. 1(*A*) (for which the initial dithizone and total mercury concentrations were $2{\cdot}75 \times 10^{-5}$M and $1{\cdot}0 \times 10^{-5}$M, respectively), we calculated the value of $K_{Hg(HDz)_2}$ as shown in Table 2. This gave a mean value for 10 determinations, with hydrochloric acid concentrations in the range 0·64—2·69M, of $2{\cdot}1 \times 10^{40}$ with a standard deviation of $0{\cdot}96 \times 10^{40}$. This should be compared with the value of $4{\cdot}0 \times 10^{40}$ calculated from Pilipenko's value [3] for the product $P_{Hg(HDz)_2}K_{Hg(HDz)_2}$ (obtained by spectroscopic methods) and from our value of $P_{Hg(HDz)_2}$. The value of $\Delta G°$ at 25° for the reaction

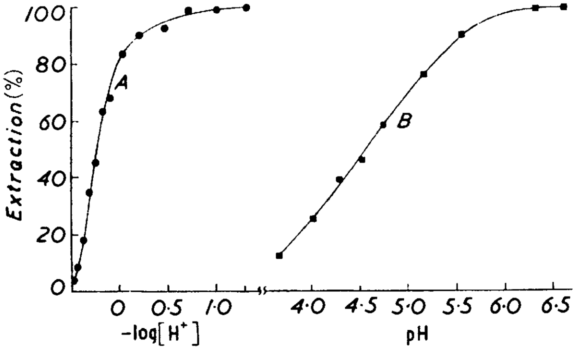

FIG. 1. *Extraction curves for mercury* (*A*) *and cobalt* (*B*).

$$Hg^{2+}{}_{(aq)} + 2HDz^-{}_{(aq)} \rightleftharpoons Hg(HDz)_{2(aq)}$$

was calculated to be —55·4 kcal./mole.

TABLE 2. *Stability constant of mercury dithizone complex.*

| $[H^+]$ (M) | $q$ | $\overline{[H_2Dz]}$ (M × $10^5$) | $\sum_0^4 K_n[Cl^-]^n$ × $10^{-15}$ | $K \times 10^{-40}$ | $[H^+]$ (M) | $q$ | $\overline{[H_2Dz]}$ (M × $10^5$) | $\sum_0^4 K_n[Cl^-]^n$ × $10^{-15}$ | $K \times 10^{-40}$ |
|---|---|---|---|---|---|---|---|---|---|
| 2·99 | $0{\cdot}044_1$ | $2{\cdot}66_5$ | $99{\cdot}3_0$ | 0·78 | 1·52 | $2{\cdot}01_5$ | $1{\cdot}14_8$ | $6{\cdot}86_2$ | 3·43 |
| 2·69 | $0{\cdot}148_5$ | $2{\cdot}48_5$ | $65{\cdot}2_9$ | 1·61 | $1{\cdot}22_4$ | 2·86 | $0{\cdot}93_4$ | $2{\cdot}93_7$ | 2·04 |
| 2·40 | $0{\cdot}222_5$ | $2{\cdot}27_8$ | $41{\cdot}5_7$ | 1·87 | 0·930 | 6·63 | $0{\cdot}53_2$ | $1{\cdot}00_9$ | 2·89 |
| 2·10 | 0·712 | $1{\cdot}82_3$ | $24{\cdot}5_2$ | 3·28 | 0·637 | 12·72 | 0·336 | $0{\cdot}235_6$ | 1·53 |
| 1·81 | 1·102 | $1{\cdot}54_4$ | $13{\cdot}6_4$ | 2·92 | 0·207 | $249{\cdot}_1$ | 0·099 | 0·0035 | 0·54 |

Note: $[Cl^-] = [H^+]$.

*Cobalt Dithizone Complex.*—(i) *Value of n in* $Co(HDz)_n$. Although previous workers [2-4] have reported a value of 2 for *n*, the evidence itemised below leads to the conclusion that $n = 3$.

(*a*) Direct titration. From 45 titrations of 0·2—43·0 μg. of cobalt(II) with dithizone, five were rejected because of errors known to be introduced by impurities. The remainder led to a value of 2·99 ± 0·02 for the dithizone to cobalt ratio in the complex (see Table 3).

(*b*) Stability constant. Values of the stability constant of the cobalt dithizone complex, $K_{Co(HDz)_n}$, were calculated from extraction curves, such as shown in Fig. 1(*B*), on the assumption that the complex formed was $Co(HDz)_2$. These values were found to vary linearly with both pH and log $\overline{[H_2Dz]}$ (see Table 4) and the slopes of the plots of log $K_{Co(HDz)_2}$ against pH and log $K_{Co(HDz)_2}$ against log $\overline{[H_2Dz]}$ were found to be always between 0·7 and 0·8 and between 1·9 and 2·2, respectively.

(*c*) Job's method. By Pilipenko's procedure [3] the results shown in Fig. 2 were obtained, giving a dithizone to cobalt ratio of 3·05 at the breaks in the curves. This is the mean of six determinations obtained in two runs, each followed at three different wavelengths.

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[11] Lindgren, Jonsson, and Sillén, *Acta Chem. Scand.*, 1947, **1**, 479.

Pilipenko obtained a value of 2·0 for this ratio. However, it appears that under certain conditions (see below) it may be possible to obtain a 2 : 1 complex, $Co(HDz)_2$, and as Pilipenko has not stated the pH at which he worked, the wavelength used for the optica density measurements, or whether or not oxygen had been excluded from the system, it is probable that his results are valid for different conditions from ours. It should also be noted that Pilipenko did not give any experimental points between the volume ratios 6·7 : 3·3 (2 : 1) and 8·0 : 2·0 (4 : 1).

TABLE 3. *Titration of cobalt*(II) *with dithizone*

| pH | $\overline{[H_2Dz]}$ (M × $10^5$) | Cobalt added (μg.) | Titre (ml.) | Ratio $H_2Dz$ : Co | No. of dtmtns. | pH | $\overline{[H_2Dz]}$ (M × $10^5$) | Cobalt added (μg.) | Titre (ml.) | Ratio $H_2Dz$ : Co | No. of dtmtns. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6·4 | 5·11 | 43·0 | 41·2$_8$ | 2·89 | 1 | 6·7 | 4·42 | 4·00 | 4·55 | 2·96 | 1 |
| 6·2 | 5·11 | 17·9 | 17·0$_5$ | 2·87 | 1 | 6·6 | 3·62 | 3·59 | 5·08 | 3·02 | 1 |
| 6·8 | 3·62 | 10·4$_2$ | 14·9$_5$ | 3·06 | 1 | 6·6 | 4·12 | 3·59 | 4·48 | 3·03 | 1 |
| 6·4 | 4·42 | 10·2$_0$ | 11·4$_9$ | 2·94 | 1 | 6·7 | 1·92 | 2·00 | 5·35 | 3·03 | 4 |
| 6·2 | 3·62 | 9·95 | 13·7$_8$ * | 2·96 * | 2 * | 6·7 | 2·30 | 2·00 | 4·46 | 3·02 | 2 |
| 6·9 | 5·11 | 9·95 | 9·81 | 2·98 | 2 | 6·7 | 2·84 | 2·00 | 3·59 | 3·01 | 4 |
| 6·8 | 2·84 | 9·89 | 17·6$_3$ | 2·99 | 6 | 6·8 | 1·92 | 1·20 | 3·24$_2$ | 3·06 | 1 |
| 6·7 | 4·42 | 9·89 | 11·3$_0$ | 2·98 | 4 | 6·7 | 1·92 | 1·00 | 2·67$_8$ | 3·03 | 3 |
| 6·2 | 5·11 | 5·98 | 5·83 | 2·94 | 1 | 6·8 | 1·92 | 0·80 | 2·09$_6$ | 3·02 | 1 |
| 6·8 | 3·62 | 5·18 | 7·08 | 2·92 | 1 | 6·8 | 1·92 | 0·50 | 1·55$_9$ | 3·53 | 2 † |
| 6·8 | 4·12 | 5·18 | 6·28 | 2·95 | 2 | 6·9 | 1·92 | 0·20 | 0·63$_5$ | 3·59 | 3 † |

* Where more than one determination was carried out under the same conditions the titres and ratios given are mean values.

† Rejected because sigmoid titration curves were obtained which showed impurities to be present.

TABLE 4. *Variation of the apparent equilibrium constant for* $Co(HDz)_2$ *with* pH *and with log* $\overline{[H_2Dz]}$.

| pH | $q$ | log $\overline{[H_2Dz]}$ | $K_{Co(HDz)_2}$ ($\times 10^{-13}$) | log $K_{Co(HDz)_2}$ | $K' \times 10^{-24}$ |
|---|---|---|---|---|---|
| 4·04 | 0·351 | −4·46 | 12·42 | 14·09 | 2·50 |
| 4·30 | 0·662 | −4·55 | 8·38 | 13·92 | 2·42 |
| 4·52 | 0·866 | −4·58 | 4·03 | 13·61 | 1·61 |
| 4·74 | 1·417 | −4·66 | 2·86 | 13·46 | 1·64 |
| 4·95 | 2·218 | −4·73 | 2·01 | 13·30 | 1·60 |
| 5·16 | 3·32 | −4·80 | 1·30 | 13·11 | 1·53 |
| 5·56 | 10·02 | −4·95 | 0·838 | 12·92 | 1·92 |
| 6·27 | 112·8 | −5·08 | 0·433 | 12·64 | 2·02 |
| 6·81 | 1025 | −5·10 | 0·326 | 12·51 | 1·75 |

Mean value of $K' = 1{\cdot}89 \times 10^{24}$ with standard deviation of $0{\cdot}32 \times 10^{24}$.

By using Miyakawa and Uemura's procedure,[4] the results shown in Fig. 3 were obtained spectroscopically, giving a dithizone to cobalt ratio of 2·83 (average of six determinations). Following the titration radiochemically at pH 6·6 led to a dithizone to cobalt ratio of 2·94. These values should be compared with the value of 2·0 given by Miyakawa and Uemura.

(*d*) Absorption spectrum. The absorption spectrum of a carbon tetrachloride solution of the complex [assayed to be $Co(HDz)_{2{\cdot}97}$ radiochemically] is shown in Fig. 4. This does not appear to contain any absorption bands due to free dithizone, and differs little in shape from other published absorption spectra for the cobalt dithizone complex.[4] The difference in the calculated molar extinction coefficient arises because we have based our figures on $Co(HDz)_3$, whereas others have used $Co(HDz)_2$. The similarity of our spectrum to those of earlier workers does not necessarily mean that the complexes previously studied have been the same as our $Co(HDz)_3$, although it is suggestive.

(*e*) Analysis. The results of analysis of two different samples, prepared independently, are shown in Table 5. They show that the specimens cannot be $Co(HDz)_2$, and agreement with the theoretical figures for $Co(HDz)_3$ is reasonable. It is therefore fair to conclude that, whereas there may be some cobalt(II) impurity present in the prepared complexes, there is no doubt that the compound is substantially cobalt(III). This is confirmed by the magnetochemical evidence.

(*f*) Magnetochemical evidence. Since cobalt(II) complexes are expected to have one unpaired *d* electron present, they should be paramagnetic. In fact, the prepared cobalt dithizone complex was found to have an almost zero (0·10 ± 0·15 Bohr magneton) paramagnetic moment. This should be compared with the very small diamagnetic moment expected for cobalt(III) complexes and the 1·73 Bohr magneton paramagnetic moment expected for cobalt(II) complexes. Again, one must come to the same conclusion as in the preceding paragraph.

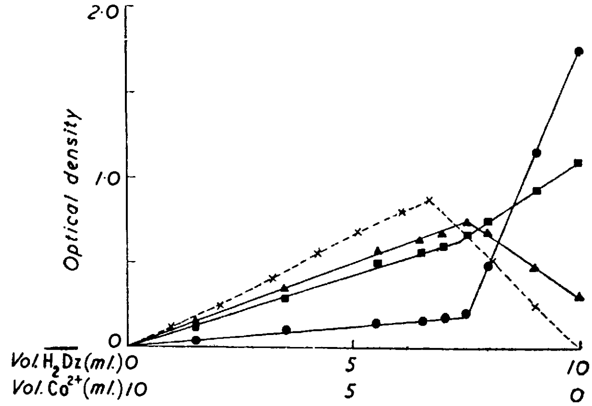

FIG. 2. *Determination of* Co : Dz *ratio by Job's method.*
● 6200 Å, ■ 5500 Å, ▲ 5100 Å, × Pilipenko's results.

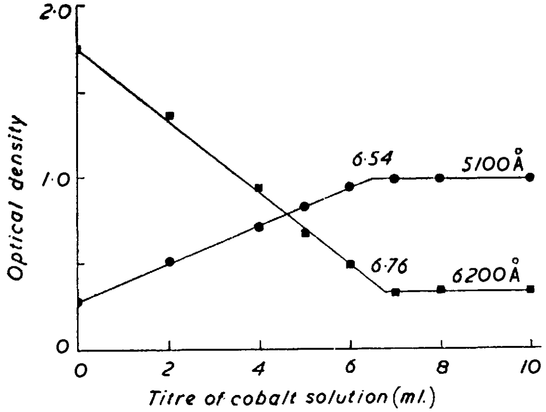

FIG. 3. *Titration of* 20 *ml. of dithizone in carbon tetrachloride* ($5{\cdot}58 \times 10^{-5}$M) *with aqueous* $Co^{2+}$ ($5{\cdot}58 \times 10^{-5}$M) *at* pH 6·9.
■ 6200 Å, ● 5100 Å.

TABLE 5. *Analyses of cobalt dithizone complexes* (% *by wt.*).

| | Calc. for | | Found | |
|---|---|---|---|---|
| | $Co(HDz)_2$ | $Co(HDz)_3$ | Sample 1 | Sample 2 |
| C ............................ | 54·82 | 56·78 | 55·29 | 57·22 |
| H ............................ | 3·89 | 4·03 | 4·62 | 4·21 |
| Co ............................ | 10·35 | 7·15 | 6·5,[a] 6·4 [b] | $6{\cdot}4_5$ [b] |
| S ............................ | 11·26 | 11·66 | 10·96 | — |

[a] Gravimetrically from the residue left after analysis for carbon, hydrogen, and sulphur. [b] By electrodeposition from a separate portion of the sample.

(*g*) Evidence for $Co(HDz)_2$. Despite all the above evidence for a 3 : 1 complex, there were two sets of results which apparently supported the formation of a 2 : 1 complex. These were that (*A*) the plot of log *q* against —log [$\overline{H_2Dz}$] (*p*L) at constant pH [Fig. 5(*A*)] was a straight line of slope —1·90, and (*B*) the plot of log *q* against pH at constant [$\overline{H_2Dz}$] was a straight line of slope 1·96 [Fig. 5(*B*)].

According to Irving *et al.*[12] the values of the slopes of these plots are identical with the value of $n$, provided complicating side reactions do not occur. Observation ($B$) does not necessarily require a 2 : 1 complex. In the formation of $Co(HDz)_2$, $Co(HDz)_2,H_2Dz$, and $Co(HDz)_3$ only two hydrogen ions are produced (see below) and hence the log $q$–pH plot does not indicate whether 2 or 3 dithizone molecules react with each $Co^{2+}$ ion. However, plot ($A$) can only support the formation of a 2 : 1 complex unless the activity coefficients of cobalt in the two phases vary significantly throughout the course of the extraction. It should be noted, however, that in ($A$) the ratio of $[\overline{Co(HDz)_n}]$ to $[\overline{H_2Dz}]$ was at least 1 : 35. It appears that this large excess of dithizone (which is a reducing agent) can prevent the oxidation of cobalt in the complex to the tervalent state. From the data of Fig. 5($A$), a value of $K_{Co(HDz)_2}$ was calculated, by use of a similar relation to equation (6), to be $2{\cdot}6 \times 10^{13}$. This agrees with Pilipenko's value[3] of $K_{Co(HDz)_2}P_{Co(HDz)_2} = 2 \times 10^{17}$ *i.e.*, $K_{Co(HDz)_2} = 2 \times 10^{13}$.

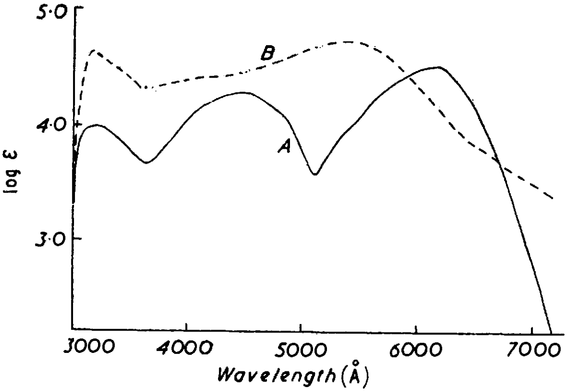

FIG. 4. *Absorption spectra of* ($A$) *dithizone and* ($B$) *the cobalt dithizone complex.*

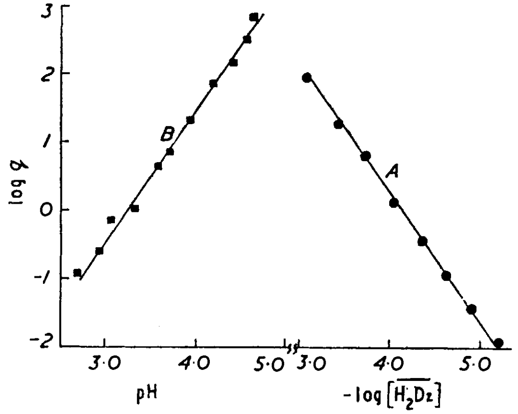

FIG. 5. *Plots of* ($A$) log $q$ *against* $-\log [\overline{H_2Dz}]$ *at constant* pH *and* ($B$) log $q$ *against* pH *at constant dithizone concentration.*

(ii) *Partition coefficient.* The results obtained from partition measurements are given in Table 6. The partition coefficient of the cobalt dithizone complex was calculated by use of an equation analogous to equation (4). The mean values at 15°, 25°, and 34·8° are respectively $0{\cdot}84 \times 10^4$, $1{\cdot}07 \times 10^4$, and $0{\cdot}97 \times 10^4$, but the differences are not significant. A value of $1{\cdot}0 \times 10^4$ has been used in all subsequent calculations in the temperature range 15—35°. The ionic strength was kept in the range 0·003—0·03 in all determinations.

(iii) *Stability constant.* When calculating the stability constant of the cobalt dithizone complex it was assumed that only two hydrogen ions were liberated during the formation of a 3 : 1 complex. This is supported by the results of several extraction runs done in the

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[12] Irving, Rossotti, and Williams, *J.*, 1955, 1906.

TABLE 6. *Partition coefficients of the cobalt dithizone complex between water and carbon tetrachloride.*

| $T$ | pH | Initial $[Co^{2+}]$ (M × $10^5$) | Activity of 5 ml. of organic phase (counts/min.) 1st extraction | 2nd extraction | $P_{Co(HDz)_3}$ ($\times 10^{-3}$) |
|---|---|---|---|---|---|
| 25·0° | 5·54 * | 1·76 | 12,330 ± 71 | 78·6 ± 5·5 | 15·78 |
| 25·0 | 6·51 ‡ | 1·76 | 12,290 ± 71 | 79·7 ± 5·5 | 15·30 |
| 25·0 | 6·56 † | 1·13 | 17,650 ± 102 | 234·0 ± 8·2 | 7·43 |
| 25·0 | 6·60 † | 1·82 | 11,110 ± 84 | 104·6 ± 6·0 | 10·53 |
| 25·0 | 7·04 ‡ | 2·55 | 4690 ± 49 | 46·4 ± 2·8 | 10·01 |
| 25·0 | 7·65 ‡ | 2·55 | 4790 ± 48 | 59·5 ± 8·1 | 7·94 |
| 25·0 | 7·80 ‡ | 1·76 | 11,860 ± 69 | 154·0 ± 8·8 | 7·58 |
| 15·5 | 6·81 † | 1·76 | 13,290 ± 77 | 187·0 ± 6·1 | 7·00 |
| 15·5 | 6·90 † | 1·82 | 10,930 ± 83 | 128·0 ± 5·9 | 8·44 |
| 15·5 | 7·61 ‡ | 1·76 | 13,420 ± 78 | 137·0 ± 6·0 | 9·69 |
| 34·8 | 7·65 ‡ | 1·76 | 12,650 ± 73 | 153·0 ± 6·0 | 8·17 |
| 34·8 | 7·81 ‡ | 1·76 | 13,610 ± 79 | 121·0 ± 5·9 | 11·15 |

Buffers: Ammonium chloride (*), sodium acetate (†), and ammonium chloride–ammonia (‡).

presence of a slight excess of dithizone [Fig. 1(*B*)]. The experimental points can be represented by an equation of the form

$$\log q = \text{Const.} + 2\text{pH} + (3{\cdot}0_5 \pm 0{\cdot}2) \log [\overline{H_2Dz}] \quad . \quad . \quad . \quad (8)$$

The above results are satisfied by any of the following reactions (all in the presence of $\overline{H_2Dz} \rightleftharpoons H_2Dz \rightleftharpoons H^+ + HDz^-$):

(*a*) No oxidation:

$$Co^{2+} + 2HDz^- + H_2Dz \rightleftharpoons Co(HDz)_2,H_2Dz \rightleftharpoons \overline{Co(HDz)_2,H_2Dz} \quad . \quad (9a)$$

$$Co^{2+} + 2HDz^- \rightleftharpoons Co(HDz)_2 \rightleftharpoons \overline{Co(HDz)_2};$$

$$\overline{Co(HDz)_2} + \overline{H_2Dz} \rightleftharpoons \overline{Co(HDz)_2,H_2Dz} \quad (9b)$$

(*b*) Reaction accompanied by oxidation:

$$Co^{2+} + 2HDz^- + H_2Dz + \tfrac{1}{4}O_2 \rightleftharpoons Co(HDz)_3 + \tfrac{1}{2}H_2O;$$

$$Co(HDz)_3 \rightleftharpoons \overline{Co(HDz)_3} \quad (9c)$$

As in (9*a*) then $\overline{Co(HDz)_2,H_2Dz} + \tfrac{1}{4}O_2 \rightleftharpoons \overline{Co(HDz)_3} + \tfrac{1}{2}H_2O$ . . . . (9*d*)

$$Co^{2+} + 2HDz^- \rightleftharpoons Co(HDz)_2 \rightleftharpoons \overline{Co(HDz)_2};$$

$$\overline{Co(HDz)_2} + \overline{H_2Dz} + \tfrac{1}{4}O_2 \rightleftharpoons \overline{Co(HDz)_3} + \tfrac{1}{2}H_2O \quad (9e)$$

Of the five reactions postulated, it appears that one of the three involving the oxidation of cobalt(II) to cobalt(III) in the complex is to be favoured because: (i) most complexes of cobalt(II) are rapidly oxidized to the corresponding cobalt(III) complex, even in macro-concentrations, *e.g.*, West[13] found it necessary to use nitrogen atmospheres when studying the exchange of $Co^{2+}$ with *NN'*-disalicylidene-ethylenediaminecobalt(II) as this, and similar compounds,[14] rapidly absorb oxygen from the air to form a cobalt(III) complex; (ii) the rate of extraction of cobalt(II) with dithizone is greatly retarded by the presence of sulphur dioxide [aqueous sulphur dioxide solutions were used to preserve the dithizone solutions and this slow rate was noted only when a concentrated (10%) sulphur dioxide solution was used instead of the usual 1% solution]; (iii) while the formation of the cobalt dithizone complex does not occur until the pH is in the range 4—6 (with dithizone concentrations of 4 × $10^{-5}$M), the complex is not extracted to any detectable extent from the organic phase by strong acid solutions, *e.g.*, concentrated hydrochloric acid, even after 30—40 minutes' shaking: this indicates that some step of the reaction is not readily reversible and this is most likely the oxidation step; and (iv) magnetic evidence suggests that the compound is a complex of cobalt(III).

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[13] West, *J.*, 1954, 395.

[14] Calvin, Bailes, and Wilmarth, *J. Amer. Chem. Soc.*, 1946, **68**, 2254.

Of the reactions which involve an oxidation step, two (9*d* and 9*e*) postulate the oxidation as occurring in the organic phase. Although this cannot be excluded, it would probably require the formation of ionic species in non-polar carbon tetrachloride, which is energetically unfavourable. Hence it appears that the formation of $Co(HDz)_3$ probably occurs *via* reaction (9*c*), with the oxidation occurring in the aqueous phase. The equilibrium constant for this reaction, $K'$, is given by:

$$K' = \frac{[\overline{Co(HDz)_3}][H^+]^2[H_2O]^{\frac{1}{2}}P_a{}^3}{[Co^{2+}][\overline{H_2Dz}]^3[O_2]^{\frac{1}{4}}K_a{}^2P_{Co(HDz)_3}} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Using this equation and the data of Fig 1(*B*), for which the initial cobalt and dithizone concentrations were $1{\cdot}13 \times 10^{-5}$M and $4{\cdot}19 \times 10^{-5}$M, respectively, and with a constant oxygen concentration (in the aqueous phase) of $2{\cdot}5 \times 10^{-4}$M,[15] we found the mean value of $K'$ to be $(1{\cdot}89 \pm 0{\cdot}32) \times 10^{24}$. The constancy of $K'$, shown in Table 4, for different experiments is additional support for the equilibrium postulated. This value of $K'$ corresponds to a free energy of reaction of $\Delta G_{25} = -31{\cdot}8$ kcal./mole. It must be emphasised that, although this value of $K'$ refers to a state of apparent equilibrium, yet under our conditions it is quite likely that the oxidation–reduction step is almost irreversible. An analogy can be drawn between this system and cobalt sulphide, which requires neutral or slightly alkaline conditions for precipitation but is insoluble in dilute hydrochloric acid (2M). This is due to oxidation by atmospheric oxygen to form a mixture of cobalt(II) and cobalt(III) sulphides.

*Structure of Metal Dithizone Complexes.*—For reactions of the type

$$M^{n+} + nL^- \rightleftharpoons ML_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

it has been shown [16] that

$$\Delta G^\circ_{ML_n} = -\boldsymbol{R}T \ln (K/K_H{}^n) + \Delta G^\circ_{M^{n+}} \quad . \quad . \quad . \quad . \quad (12)$$

where $\Delta G^\circ_{ML_n}$ is the standard free energy of $ML_n$(aq) with respect to that of the free acid, HL(aq); $\Delta G^\circ_{M^{n+}}$ is the standard free energy of $M^{n+}$(aq); $K$ is the stability constant of reaction (11), and $K_H$ that for the dissociation of HL in aqueous solution. There are a number of limitations in the application of equation (12) to experimental data, which have been discussed elsewhere.[16] Nevertheless, bearing these limitations in mind, we may evaluate $\Delta G^\circ_{ML_n}$ from $K$, $K_H$, and $\Delta G^\circ_{M^{n+}}$. It has already been shown [16] that the plot of $\Delta G^\circ_{M(HDz)_2}$ against $\Delta G^\circ_{M^{n+}}$ is quite abnormal. This deviation requires a difference in the product $P_{M(HDz)_2}K_{M(HDz)_2}$ from that expected by a factor of about $10^{25}$ for mercury and by about $10^{10}$ for copper. These increased stabilities can, however, be related to structural features, evidence for which was obtained by infrared spectroscopy. The observed N–H stretching frequencies for the compounds studied are quoted in Table 7. The following conclusions emerge.

TABLE 7. *Infrared investigation of metal dithizone complexes in carbon tetrachloride solution.*

| Compound | $Cu(HDz)_2$ | CuDz | $Hg(HDz)_2$ | $Co(HDz)_3$ | $H_2Dz$ |
|---|---|---|---|---|---|
| Frequency (cm.$^{-1}$) of N–H stretching motion | 3219 | Not detectable | 3272 | 3255 | 3139 |

(i) *Copper dithizone complexes.* It should first be noted that the compound giving an analysis corresponding to CuDz (see Table 8) shows no detectable N–H stretching frequency. This is not surprising, since this compound is commonly written with the structure (*A*) in which both hydrogen atoms of dithizone are acidic, leaving no N–H bond in the complex. Our evidence does not, however, indicate whether or not the second co-ordination is by another nitrogen atom. As expected, the compound $Cu(HDz)_2$ shows an absorption peak due to the stretching of an N–H bond. Therefore this compound has one of the

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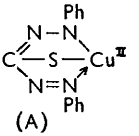
[15] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1946, p. 1396.

[16] Duncan, *Australian J. Chem.*, 1959, **12**, 356.

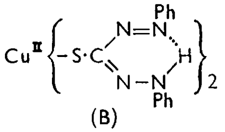
TABLE 8. *Analyses of copper and mercury dithizone complexes* (% *by wt.*).

| | CuDz | | $Cu(HDz)_2$ | | $Hg(HDz)_2$ | |
|---|---|---|---|---|---|---|
| Compound | Calc. | Found | Calc. | Found | Calc. | Found |
| C | 49·1 | 43·9, 43·9 | 54·4 | 53·0 | 43·9 | 43·3 |
| H | 3·2 | 3,3, 3·5 | 3·9 | 4·1 | 3·1 | 3·0 |
| S | 10·1 | 9·5, 9·6 | 11·2 | 10·4 | 9·0 | 8·7 |
| Metal (from ash) | 20·0 | 19·3, 19·6 | 11·1 | 11·2 | 28·2 | 29·0 |

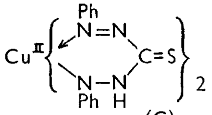
structures (*B*), (*C*), or (*D*). Of these, structure (*B*) would appear to be more likely for the following reasons: (*a*) it allows stronger hydrogen bonding and therefore a more pronounced lowering of the N–H frequency from the value for an N–H bond not involved in hydrogen bonding, *e.g.*, the value of 3326 cm.$^{-1}$ for the N–H stretching frequency in diazoaminobenzene, Ph·N:N·NHPh,[17] a suitable analogue for the dithizone system; (*b*) the hydrogen atom attached to the 1-N atom in the free dithizone molecule is hydrogen bonded also (see experimental N–H frequency of 3139 cm.$^{-1}$). The values of the N–H stretching frequencies obtained for the dithizone complexes (Table 7) show that partial hydrogen bonding of dithizone complexes occurs in the order $H_2Dz > Cu(HDz)_2 > Co(HDz)_3 > Hg(HDz)_2$, the last being very weak or non-existent; and (*c*) the hydrogen atom attached to the 2-N atom in dithizone would be expected to be more acidic than that attached to the 1-N atom, owing to the proximity of the sulphur atom. Structure (*B*) is also supported by the evidence of Irving and Bell [18] which shows that the *S*-methyl derivative of dithizone does not form complexes with metals, and it is perhaps significant that most thiols react strongly with copper and mercury. However, it is difficult to see how, in structure (*B*), the copper(II) can reach the usual co-ordination number of 4 or 6.



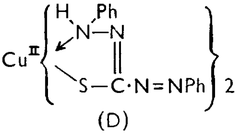
(A)



(B)



(C)



(D)

(ii) *Mercury dithizone complex.* This appears to be similar to the copper dithizone complex $[Cu(HDz)_2]$, structure (*B*), for the following reasons: (*a*) The similarity in the infrared spectrum. (*b*) The similarity in the deviations from the linear free-energy plots:[16] the deviations from linearity in this plot may be related to the varying degree of hydrogen bonding present in the complexes, those with the least hydrogen bonding having the greatest deviation. (*c*) Harding [19] has shown that, in the solid state at least, the mercury is bonded through the sulphur atom and that the structure is somewhat like structure (*D*) with the mercury–nitrogen bond being very long (2·6 Å) and hence rather weak, and that no intramolecular hydrogen bonding occurs: this agrees with our infrared measurements which indicate that there is very little, if any, hydrogen bonding in the mercury dithizone complex.

(iii) *Cobalt dithizone complex.* It should be noted first that only a single N–H stretching frequency was observed. It follows, therefore, that structures in which the third dithizone residue is bound to the cobalt atom in a different way from the other two, *e.g.*, $Co(HDz)_2(H_2Dz)$, are unlikely. This therefore supports the previous observations that oxidation of cobalt(II) to cobalt(III) has occurred. The similarity of the N–H stretching frequency to those of $Cu(HDz)_2$ and $Hg(HDz)_2$ suggests that it also has a structure similar to structure (*B*) but with fairly weak hydrogen bonding.

Thanks are offered to Miss J. T. Radford for electrochemical cobalt analyses, to Professor ~~A. N. Hambly, Mr. L. K. Dyall, and Mr. J. Allpress for infrared measurements, and to the~~ Australian Atomic Energy Commission for a Senior Research Studentship (to F. G. T.).

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[17] Dyall, personal communication.
[18] Irving and Bell, *J.*, 1954, 4253.
[19] Harding, *J.*, 1958, 4136.