[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Spectra of Solutions of Cobalt(II) Thiocyanate Complexes in 4-Methyl-2-pentanone

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Spectra were obtained for solutions of cobalt(II) thiocyanate complexes in 4-methyl-2-pentanone and were prepared variously by extraction from aqueous thiocyanate–perchlorate media and by adding $Co(ClO_4)_2$ and NaNCS to anhydrous ketone and to ketone which was first equilibrated with aqueous $HClO_4$. Results indicate that tetrahedral $H_nCo(NCS)_{2+n}Z_{2-n}$ (Z is ketone or water) complexes predominate. In the 4-methyl-2-pentanone, which was first saturated with aqueous $HClO_4$, possible evidence for 6/1 complexing was found. Studies of the spectra of solutions in the near infrared and of mulls of $Ba[Co(NCS)_4]$ in the infrared, fail to show the electronic bands predicted for $Co(NCS)_4^{=}$ by ligand-field theory. Some possible interpretations are discussed.

Various workers[1-3] have examined the absorption spectra of thiocyanato-cobalt(II) complexes in water and a number of non-aqueous solvents. Katzin[1] has presented evidence which demonstrates the existence of six-coördinate thiocyanato-aquo complexes in aqueous solutions and four-coördinate, tetrahedral complexes in several organic solvents. Recently Ballhausen and Jorgensen[4] have discussed the spectra of cobalt(II) complexes in terms of the ligand-field theory and have concluded with Katzin that the red solutions (maximum absorption at about 510 mμ) represent octahedral complexes and the blue solutions (maximum absorption at about 620 mμ) represent tetrahedral complexes.

Our own solvent extraction studies[5] indicate that the blue complexes in 4-methyl-2-pentanone contain three or four thiocyanate groups per cobalt and hence appear to agree with the previous work. However, spectra of a few of the ketone phase samples from the extraction work showed unexpectedly large absorbancies and caused us to undertake the present study.

Experimental

A Beckman model DK-2 spectrophotometer and 1 cm. or 0.1 cm. quartz cells were employed for the measurement of absorption spectra between 220 and 2000 mμ. Infrared spectra of the $Ba[Co(NCS)_4]$-Nujol mulls were measured on a Perkin–Elmer model 21 infrared spectrophotometer.

Samples of the organic phases from the extraction experiments were examined directly. Solutions for continuous variation studies were prepared by dissolving weighed amounts of $Co(ClO_4)_2$ and NaNCS in 4-methyl-2-pentanone or in the ketone which had been saturated with 1.00 *M* or 0.500 *M* $HClO_4$ solutions. $HClO_4$, the ketone and the various salts were prepared as described in the extraction study.[5]

$Ba[Co(NCS)_4]$ was prepared in solution by mixing stoichiometric amounts of $Ba(NCS)_2$ and $Co(NCS)_2$. A concentrated solution was treated with acetone and benzene until the $Ba[Co(NCS)_4]$ precipitated. Nujol mulls were prepared from this solid and the absorption spectrum was measured from 2.0 to 14.0 μ.

Results

Figures 1 and 2 illustrate the essential features of the aqueous and ketone phases from the extraction studies and correspond to the spectra attributed[1,4] to the six-coördinate and four-coördinate complexes, respectively.

Barium tetrathiocyanatocobaltate(II) was a blue solid and in water–acetone showed only the 620 mμ maximum in the 400 to 700 mμ region. Nujol mulls of this compound exhibited only the absorptions of the thiocyanate ion, in the 2.0 to 14.0 μ region, plus what is probably a small —C=N— band at 6.2 μ.[6] There were no absorption bands which could be attributed to electronic transitions in the infrared region studied.

TABLE I

CONTINUOUS VARIATION STUDIES AT VARIOUS TOTAL SALT CONCENTRATIONS IN ANHYDROUS 4-METHYL-2-PENTANONE

DATA ARE FOR 1 CM. CELLS

[Co(II)] × 10^3, *M*	A_{580}	A_{620}	A_{640}
1. $[Co(II)] + [NCS^-] = 4 \times 10^{-3}$ *M*			
2.67	0.070	0.145	0.160
2.00	.155	.370	.405
1.33	.270	.755	.820
1.00	.405	1.23	1.24
0.800	.735	1.70	1.20
.665	.640	1.42	1.02
.570	.565	1.19	0.820
.445	.440	0.900	.620
.400	.380	0.790	.570
2. $[Co(II)] + [NCS^-] = 8 \times 10^{-3}$ *M*			
5.34	0.159	0.339	0.367
4.00	.335	0.850	0.915
2.67	.500	1.37	1.50
2.00	.750	2.06	2.11
1.60	1.41	2.81	2.11
1.33	1.23	2.39	1.70
1.14	1.08	2.20	1.58
0.89	0.800	1.75	1.15
0.80	0.750	1.49	1.05

Solutions in 4-methyl-2-pentanone, containing 0.0016 *M* cobalt perchlorate and 0.0064 *M* sodium thiocyanate, were examined from 350 to 2000 mμ. In addition to the maximum at 620 mμ ($a_m = 1760$), there was a band in the near infrared with a maximum at 1310 mμ ($a_m = 242$). Further there was the beginning of a very strong band below 400 mμ, but the maximum could not be located due to the opacity of the ketone below 350 mμ. The corresponding solution in 1-propanol had a maximum at 310 mμ which was about six times as strong as the 620 band in the same solvent.[7] The spectrum in the ketone is shown in Fig. 3.

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(1) L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5659, 5455 (1950); **75**, 2830 (1953).

(2) A. K. Babko and O. F. Drako, *J. Gen. Chem.* (*U. S. S. R.*), **19**, 1809 (1949); **20**, 288 (1950); *C. A.*, **44**, 1355, 5684 (1950).

(3) M. Lehene, *Bull. soc. chim. France*, 76 (1951).

(4) C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 397 (1957).

(5) C. E. Johnson and C. H. Brubaker, Jr., paper in preparation.

(6) T. Dreisch and W. Trommer, *Z. physik. Chem.*, **37B**, 37 (1937).

(7) A. Kiss and P. Csokan, *ibid.*, **A188**, 27 (1941).

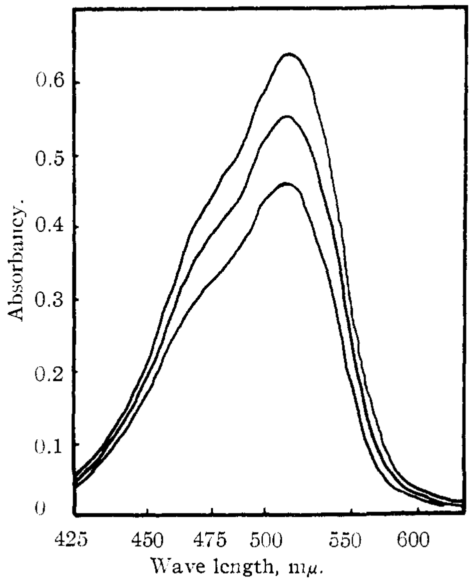

Fig. 1.—Aqueous phase spectra (1.0 cm. cells): lower curve, 0.0505 M Co(II), 0.0220 M NCS^-; middle, 0.0471 M Co(II), 0.0477 M NCS^-; 0.0405 M Co(II), 0.0748 M NCS^-.

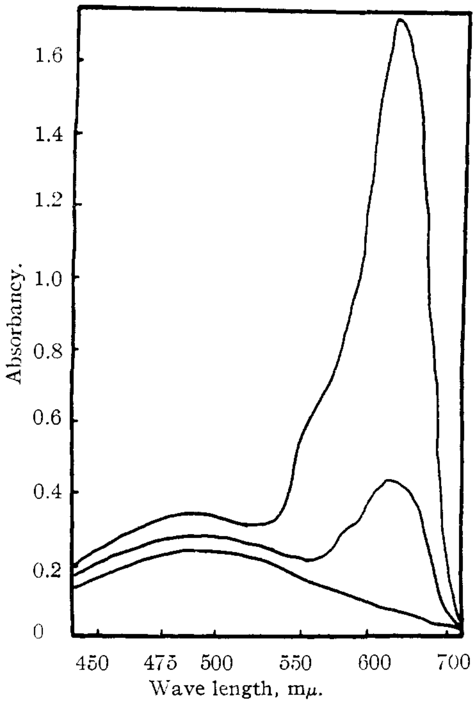

Fig. 2.—Organic phase spectra (1.0 cm. cells): lower curve, 0.0101 M Co(II), 0.0122 M NCS^-; middle, 0.0101 M Co(II), 0.0254 M NCS^-; upper, 0.0098 M $Co(II)^-$, 0.0406 M NCS^-.

A number of continuous variation studies were made at various total concentrations in 4-methyl-2-pentanone and in the ketone which was first saturated with 1.00 and 0.500 M aqueous perchloric acid. These results are given in Tables I, II and III. The purpose of saturating the solvent with $HClO_4$ was to try to duplicate, as nearly as possible, the wet organic phase of the extraction studies.

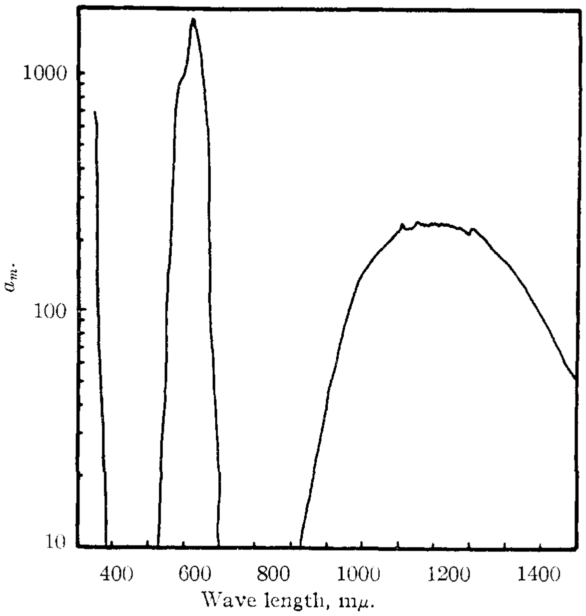

Fig. 3.—Spectrum (semi-log scale) of 0.0016 M $Co(ClO_4)_2$ + 0.0064 M NaNCS in M.I.B.K.

The results from the series in the anhydrous ketone clearly indicated complexes with three and four thiocyanates per cobalt. Further, the limiting value of the molar absorbancy index at 620 was 1920 in the 0.004 M series and 2100 in the 0.008 M series. These values are of the same magnitude as those found in the extraction work.

In the studies in 4-methyl-2-pentanone saturated with 1.00 M $HClO_4$ rather different results were found, although the visible maximum still appeared at 620 mμ. At 0.100 M total salt, continuous variation curves showed a maximum at 6/1 composition (*cf.* West and DeVries[8] for water–ethanol mixtures). In the 0.0400 M series maxima appeared at compositions of 3/1 and at about 6/1, but at 0.0300 M the only maximum appeared between 3/1 and 4/1.

In the ketone, which was saturated with 0.500 M $HClO_4$, a study at 0.0400 M total salt showed a maximum at 6/1 composition and molar absorbancy indices were higher than with the 1.00 M acid cases. However, the molar absorbancy indices were always lower in the wet ketone than in the anhydrous and did not appear to approach a limit, even when $[NCS^-]/[Co(II)]$ was 8/1 to 10/1.

Discussion

Since most previous work,[1,4] our solvent extraction studies and continuous variation in the anhydrous ketone point to the blue solutions of cobalt thiocyanates having chiefly tetrahedral complexes, the questions raised by the results of the experiments with barium tetrathiocyanatocobaltate(II) mulls and the continuous variations in the wet ketone are disturbing.

The continuous variation studies might be taken to mean that a 6/1 complex can occur in addition to the well known 3/1 and 4/1 compounds. However, Katzin and Gebert[1] have pointed out that, in

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[8] P. W. West and C. G. DeVries, *Anal. Chem.*, **23**, 334 (1951).

TABLE II

CONTINUOUS VARIATION STUDIES AT VARIOUS TOTAL SALT CONCENTRATIONS IN 4-METHYL-2-PENTANONE, SATURATED WITH 1.00 M $HClO_4$ (1 CM. CELLS)

[Co(II)] $\times 10^2$, M	A_{580}	A_{620}	A_{640}
1. $[CO(II)] + [NCS^-] = 0.100$ M			
10.0	0.060	0.022	0.020
8.00	.130	.157	.152
6.66	.338	.650	.643
5.71	.673	1.17	1.13
5.00	.83	1.76	1.67
3.33	1.70	3.90	3.82
2.50	2.05	4.70	4.39
2.00	2.64	6.23	5.70
1.43	3.40	9.25	8.10
1.11	2.80	6.25	5.50
0.91	2.75	6.11	5.35
2. $[Co(II)] + [NCS^-] = 0.0400$ M			
4.00	0.020	0.020	0.018
2.67	.044	.030	.030
2.00	.046	.045	.041
1.60	.080	.120	.120
1.33	.080	.125	.120
1.14	.145	.175	.175
1.00	.100	.175	.170
0.890	.098	.163	.163
.800	.080	.125	.120
.727	.105	.200	.200
.662	.112	.205	.200
.615	.112	.215	.220
.570	.117	.240	.240
.533	.115	.240	.240
.500	.115	.240	.240
.450	.110	.190	.185
.400	.100	.164	.159
3. $[Co(II)] + [NCS^-] = 0.0300$ M			
3.00	0.007	0.000	0.000
2.40	.020	.011	.010
1.50	.032	.041	.041
1.00	.053	.085	.085
0.750	.061	.117	.112
.600	.060	.115	.110
.424	.035	.060	.059
.333	.022	.042	.041

TABLE III

CONTINUOUS VARIATION STUDY IN 4-METHYL-2-PENTANONE SATURATED WITH 0.500 M $HClO_4$

[Co(II)] $\times 10^2$	A_{580}	A_{620}	A_{640}
$[Co(II)] + [NCS^-] = 0.0400$ M			
4.00	0.062	0.040	0.038
2.00	.076	.110	.108
1.35	.143	.275	.274
1.00	.200	.430	.433
0.800	.235	.520	.530
.660	.260	.590	.593
.570	.263	.650	.660
.450	.260	.615	.610

the case of two or three important complexes the continuous variation maximum of the lower complex may appear at less than the actual ratio and the maximum from the higher (or highest) may occur at a composition greater than the actual composition of the complex. Further, given certain relative stabilities and extinction coefficients, the two maxima and a minimum may appear.

Thus supposed 6/1 complexing may be an artifact: the result of the existence of several important complexes in the wet ketone and the resulting shift of the maximum from the 4/1 complex to compositions corresponding to 5/1 or even 6/1. Such shifts are greater than are generally noted, but the idea finds support in the result that the molar absorbancy indices do not approach limiting values in wet ketone.

According to Ballhausen and Jorgensen,[4] the 620 mμ absorption (16100 cm.$^{-1}$) should be due to a transition from the $4F(\Gamma_2)$ state to $4P(\Gamma_4)$ state. These levels arise from the splitting of the 4F and 4P states of the gaseous ion by the tetrahedral ligand-field of four thiocyanate ligands. If this assignment is correct, one would expect to find the $4F(\Gamma_2)$–$4F(\Gamma_4)$ transition in the infrared between about 1000 and 4600 cm.$^{-1}$ (10 to 2.2 μ) and the $4F(\Gamma_2)$–$4F(\Gamma_5)$ transition should appear below 2300 cm.$^{-1}$ (at 4.3 μ or longer wave lengths).

Since the predicted electronic bands could not be found in the infrared, it may be that the 620 mμ absorption should not be associated with the $4F(\Gamma_4)$–$4P(\Gamma_4)$ transition, that tetrahedral symmetry does not obtain or that this absorption does not represent a ligand-field band at all.

We first decided (influenced by the apparent six to one complexing in wet ketone) to try to interpret the spectra by assuming octahedral or tetragonal ligand fields but had no success in this venture. We then decided to consider a tetrahedral field and to assign the Γ_2–Γ_5 transition to the infrared band between 1000 and 1500 mμ (10,000–6250 cm.$^{-1}$). In that case the Γ_2–Γ_4 transition should appear between 555 and 885 mμ (18,000–11,300 cm.$^{-1}$); that is, it should be the strong visible band. The $4F(\Gamma_2)$–$4P(\Gamma_4)$ transition should be found around 370–430 mμ (27,000–23,000 cm.$^{-1}$). In the spectra in 4-methyl-2-pentanone a large absorption begins at wave lengths just below 400 mμ and the maximum appears in 1-propanol solutions at 310 mμ.

The ratio of the frequencies for the Γ_2–$\Gamma_5(\nu_1)$ and the Γ_2–Γ_4 (ν_2) transitions should be $\nu_2/\nu_1 = 1.8$, but a value of about 2.1 is found. This suggests a larger separation of levels than is predicted, but normally smaller separations are observed.[9] Moreover, Katzin[10] has presented evidence that the 310 mμ band is a modified thiocyanate band.

It is thus suggested that the absorption at 620 mμ does not represent a ligand-field band at all and that some other cause must be sought.

The details (both of shape and of the magnitude of a_m) of the spectra of the organic solutions from solvent extraction studies, resemble more closely those of the dry ketone spectra than those of the wet ketone spectra, although they are certainly wet solutions. Thus it is suggested that the solutions in 4-methyl-2-propanone saturated with aqueous perchloric acid, are different because of the presence of perchloric acid and not because of water. More-

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[9] D. A. Brown, *J. Chem. Phys.*, **28**, 67 (1958).

[10] L. I. Katzin, *ibid.*, **20**, 1165 (1952).

over, in the solvent extraction studies, the highest absorbancy indices are associated with the lowest hydrogen ion concentrations, and in the continuous variation series the same trend is noted.

Katzin[11] feels that thiocyanic acid should be stronger in coördination than the ion pair (Na^+-NCS^-) and hence sixfold coördination should be more likely in the system $Co(ClO_4)_2 + NaNCS$ in the presence of perchloric acid. Thus one may be able to rationalize the six to one complexing (if such does indeed occur) in terms of the effect of the strong acid ($HClO_4$), but the fundamental question of the source of the 620 mμ absorption is left unanswered.

One possible explanation lies in a charge transfer process. The 620 mμ absorption may be the result of transfer of an electron along one of the thiocyanate ligands to the solvent. The intensity, but not the wave length, might depend on the number of thiocyanates present, as is observed. In the absence of tests of such an hypothesis, however, it is probably best to withhold judgment.

Acknowledgment.—The authors thank J. C. Sternberg for the many helpful suggestions he has given.

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[11] L. I. Katzin, private communication.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Zirconium–Hydrogen System: Some Thermodynamic Properties from a Heat Content Study[1]

BY THOMAS B. DOUGLAS

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The relative heat contents of zirconium and five zirconium hydrides (24–52 atomic % hydrogen) were precisely measured over the range 0–900°. Appreciable hysteresis was observed only near the eutectoid temperature. After developing a method generally applicable to heterogeneous systems, the heats of isothermal hydriding throughout most of the range of temperature and composition investigated were derived. Several of the boundaries of the phase diagram also were derived from the thermal data and are found to be in reasonably good agreement with the published results found by other methods. The energies and relative stabilities of the high temperature crystalline forms are discussed qualitatively after estimating their disorder entropies.

Investigations of several alloy-like hydride systems have been reported by many authors during the past few years. In the case of the zirconium–hydrogen system recent investigations of equilibrium hydrogen pressures,[2-4] diffusion of hydrogen,[5] high temperature X-ray diffraction[6] and neutron diffraction[7] have provided valuable if somewhat conflicting evidence concerning the crystal structures, energies and limits of composition of the existing phases. In this paper a number of energy relations of this system are derived from recently measured heat contents of a few compositions. It has been possible to correlate extensively the thermal results with some of the reported equilibrium values and to examine critically many discrepancies found. The evaluation of a thermodynamic property by several independent methods is particularly desirable in the case of *solid* systems, where equilibration is often slow and frequently not achieved.

As a multi-phase material changes temperature, physical or chemical changes often occur whose heats of reaction constitute a major part of the energy change. If the components are virtually immiscible at some temperature but become miscible or otherwise interact reversibly at another temperature, it is possible to measure the change in heat content of such a mixture over the given temperature range, then repeat the measurement on the components in a separated condition so that they have no opportunity to interact, and from the difference alone find the heat of the reaction occurring when the mixture changes temperature. The precise heat content data used in this paper determine the *differences* among the heats of a number of such reactions in the zirconium–hydrogen system, and assuming one of the values as determined by another method, all the other heats of reaction can be evaluated. Similarly, a number of equilibria, some already known at one temperature, were evaluated over a range of temperature by use of the thermal data.

Experimental

The total impurities and corrected hydrogen contents of the zirconium and the five samples of zirconium hydrides whose heat contents were measured are given in Table I.

Sample 1 was crystal-bar zirconium obtained from the U. S. Bureau of Mines, Albany, Ore. Samples 2 and 6 were supplied by the U. S. Air Force, Wright Air Development Center, where their hydrogen contents were determined (to an estimated accuracy of ±0.5% of the hydro-

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[1] (a) Presented before the Division of Physical and Inorganic Chemistry, 133rd National American Chemical Society Meeting, San Francisco, Calif., April, 1958. (b) The measurements of heat content were sponsored by the Wright Air Development Center, Air Research and Development Command, United States Air Force, under Delivery Order No. AF 33(616)56-21, Project No. 7360. (c) Complete experimental details and data have been given by T. B. Douglas and A. C. Victor, *J. Research Natl. Bur. Standards*, **61**, 13 (1958) (RP 2878).

[2] E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, **101**, 474 (1954); *J. Metals*, **7**, 136 (1955).

[3] R. K. Edwards, P. Levesque and D. Cubicciotti, THIS JOURNAL, **77**, 1307 (1955).

[4] C. E. Ells and A. D. McQuillan, *J. Inst. Metals*, **85**, (Part 3), 89 (1956).

[5] C. M. Schwartz and M. W. Mallett, *Trans. Amer. Soc. Metals*, **46**, 640 (1954).

[6] D. A. Vaughan and J. R. Bridge, *J. Metals*, **8**, 528 (1956).

[7] R. E. Rundle, C. G. Shull and E. O. Wollan, *Acta Cryst.*, **5**, 22 (1952).