# **848.** *The Infrared Spectra of Cobalt*(III) *Ethylenediamine Complexes. Part I. Vibrations of the Ethylenediamine Chelate Ring.*

By M. E. BALDWIN.

The infrared absorption spectra of some ethylenediamine complexes of tervalent cobalt have been measured in the region 500—4000 cm.$^{-1}$. Assignment of the bands arising from vibrations of the amino-group has been made by observing the shifts resulting on deuteration. A study of the region 850—900 cm.$^{-1}$ provides a means for differentiation of *cis*- and *trans*-isomers of bisethylenediamine complexes.

IN the solid state the vibrational modes of metal–chelate rings are affected by (i) the orientation of the chelate molecules around the metal atom, (ii) the spatial configurations of the individual chelate molecules, and the non-bonded interactions between them, and (iii) ionic interaction or hydrogen bonding between the anion and the cation in a salt.

The present work was undertaken in order to discover whether infrared spectra could be used to distinguish between *cis*- and *trans*-arrangements of the chelate rings about cobalt, and the extent to which non-bonded and ionic interactions could be detected. A large number of ethylenediamine complexes of tervalent cobalt has been studied in paraffin mulls in the solid state. The measured frequencies of the absorption bands of compounds of the types *cis*- and *trans*-$[Co(en)_2Cl_2]X$ and $[Co(en)_3]X_3$ are given in Tables 1, 2, and 3.

TABLE 1. *Frequencies* (*cm.*$^{-1}$) *of compounds of the type* cis-$[Co(en)_2Cl_2]X$, *where* X = Cl, Br, I, SCN, $ClO_4$, $\frac{1}{2}S_2O_6$.

| Cl | Br | I | SCN | $ClO_4$ | $S_2O_6$ | Cl | Br | I | SCN | $ClO_4$ | $S_2O_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3460sh | 3472m | | | | | 1163m | 1160w | 1164m | 1143s | | |
| 3425s | 3425s | | | | | 1134s | 1133s | 1136w | | | |
| | | | | | | 1117s | 1115s | 1117s | | | |
| 3274sh | 3266m | 3257m | 3268m | 3300m | | 1111sh | 1111sh | 1111s | 1109s | | |
| 3266m | | | | 3266sh | | 1098m | 1086m | 1099sh | 1096s | | |
| 3195s | 3195s | 3215s | 3195s | 3279s | | 1064sh | 1064sh | | 1050vs | | |
| 3165sh | 3165sh | | | 3215sh | | 1058s | 1058vs | 1058vs | 1018sh | | |
| 3096m | 3096m | 3125m | 3115m | 3125m | | 1010sh | 1018sh | | | | |
| | | | | | | 1005m | 1005m | 1005s | | | |
| | | | 2058s | | | 999sh | 990sh | 999sh | 998m | | |
| | | | | | | | | | 938w | | |
| 1634s | 1626s | 1658s | | | 1600vs | | | | 930w | | |
| 1587sh | 1582sh | 1563sh | 1585sh | 1587sh | | 900m | 896m | 891s | 893w | 894m | 899m |
| 1565s | 1565sh | 1558s | 1558m | 1570vs | 1572vs | 876m | 871m | 876m | 879m | 877m | 893sh |
| 1541sh | 1560s | 1538sh | 1538sh | 1560sh | | | | 863m | | | 876m |
| | 1546sh | | | | | 788s | 775s | 780vs | 801m | 782sh | 775s |
| | | | | | | 770s | 761s | 759s | 746s | 769vs | 754w |
| 1305m | 1318m | 1312m | 1316sh | | | | 733m | 741w | | 757s | |
| | | | 1302m | | | 714m | 722m | 719s | | | |
| 1299sh | 1297sh | 1290w | | | | | 704m | 699w | 690m | 690w | 695w |
| 1285m | 1284m | 1274sh | 1274m | | | | | | | 620vs | 692m |
| 1272sh | 1271sh | 1267m | | | | 549s | 570sd | 585sd | 578s | 585s | 570vs |
| 1212s | 1208m | 1192m | 1190w | | | 443s | | 565sd | 565s | 571s | |
| 1200s | 1193m | 1188m | | | | | | | | 565s | |
| | | 1176m | 1163s | | | | | | | 556s | |

* For key to intensities, see footnote to Table 3.

*Assignment of the Absorption Bands of the Ethylenediamine Cobalt Ring System.*—(a) *Vibrations of the* $NH_2$ *group.* The principal modes of vibration of the $NH_2$ group are symmetrical stretching, asymmetrical stretching, bending, wagging, twisting, and rocking. An assignment of the bands arising from these vibrations has been made by observing the shifts resulting on the deuteration of the following complex ions: $[Co(en)_3]Cl_3$, $[Co(en)_3](SCN)_3$, *trans*-$[Co(en)_2Cl_2]Cl$, and *trans*-$[Co(en)_2Cl_2]SCN$ (cf. Tables 4 and 5).

Bands in the regions 3000—3300, 1550—1580, 1160—1120, 1015—995, and 800—740 cm.$^{-1}$ showed isotope shifts and may be assigned to the vibrations of the $NH_2$ group.

TABLE 2. *Frequencies* (*cm.*$^{-1}$) *of compounds of the type* trans-$[Co(en)_2Cl_2]X$, *where* X = Cl, Br, I, SCN, NCO, $ClO_4$, $\frac{1}{2}S_2O_6$, $NO_3$.

| Cl | Br | I | SCN | NCO | $ClO_2$ | $S_2O_6$ | $NO_3$ |
|---|---|---|---|---|---|---|---|
| | | | | | | | 3505w |
| | | | | | | | 3425sh |
| 3274m | 3268sh | 3247vs | 3247m | 3328m | 3289s | 3311m | 3279sh |
| 3250s | 3247s | 3195sh | 3226s | 3226s | 3263s | 3257sh | 3257s |
| 3165m | 3167s | 3170s | 3190m | 3185w | 3221s | 3226s | 3226sh |
| 3125sh | 3120sh | 3115sh | 3120m | 3115w | 3185w | 3145s | 3175s |
| 3077s | 3086s | 3096s | | | 3115w | | |
| | | | 2046vs | 2137vs | | | |
| 1591s | 1592s | 1587s | 1585vs | 1592s | 1587s | 1590sh | 1603vs |
| | | 1582sh | | 1582sh | 1572sh | 1567vs | |
| 1309m | 1314s | 1312m | 1312s | 1314m | | | |
| 1290w | 1289w | 1285w | 1279s | 1302sh | | | |
| 1271s | 1271s | 1269m | | 1285m | | | |
| 1206s | 1206sh | 1206m | 1200w | 1196m | | | |
| | 1203s | 1190sh | 1156w | | | | |
| | | | 1147w | | | | |
| 1120vs | 1114vs | 1110vs | 1110vs | 1111vs | | | |
| 1100vs | 1101vs | 1104vs | | | | | |
| 1053vs | 1053vs | 1053vs | 1050vs | 1053vs | | | |
| 1004vs | 1006vs | 1003s | 1008s | 1011w | | | |
| 994vs | 997vs | 994s | 993s | 998m | | | |
| | | | 934m | | | | |
| | | | 927m | | | | |
| 888m | 889m | 888m | 892s | 898m | 888m | 887m | 888s |
| | | | | 889sh | 881sh | | 824s |
| 808s | 806s | 800s | 789m | 820m | 789m | 778vs | 810vs |
| 754m | 723m | 719m | 754s | 769vw | 743w | 735w | 727s |
| | | | 706m | 623vs | 720w | 704w | |
| | | | | 616vs | 620vs | | |
| 587vs | 586vs | 585s | 588vs | 592vs | 585s | 588sd | 588vs |

TABLE 3. *Frequencies* (*cm.*$^{-1}$) *of compounds of the type* $[Co(en)_3]X_3$, *where* X = Cl, Br, I, SCN, $ClO_4$.

| Cl | Br | I | SCN | $ClO_4$ | Cl | Br | I | SCN | $ClO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| 3484m | 3503m | 3509w | | | 1159vs | 1155vs | 1152vs | 1152vs | |
| 3425m | 3413m | 3436w | | | 1125s | 1121s | 1117sh | 1129sh | |
| 3215m | 3205m | 3175md | 3215sd | 3284m | 1114sh | 1111sh | 1109s | | |
| 3165sh | 3175sh | 3106md | 3177sh | 3205s | 1058vs | 1057vs | 1059vs | 1054s | |
| 3086m | 3089m | | 3077sd | 3165sh | | | 1052vs | 1037sh | |
| | | | 2066vs | 3086s | 1005w | 1018w | 1020w | 1005w | |
| | | | 2033vs | | | 1004w | 998w | 945w | |
| 1618m | 1613m | 1616m | 1600sh | 1616m | 895m | 895m | 888m | 886m | 892m |
| 1600sh | 1582s | 1580s | 1582s | 1582sh | 879m | 882m | 877sh | 876m | 881m |
| 1585s | 1563sh | 1538sh | 1560sh | 1558s | | | 868m | | |
| | 1553s | 1511s | 1538sh | | 781s | 783vs | 793m | 813sh | 803sh |
| 1326s | 1323s | 1318s | 1321w | | | | 775s | 800s | 788s |
| 1302w | 1300w | 1295s | 1302w | | | | | 785sh | 769sh |
| 1277m | 1276m | 1267w | 1284m | | 714w | 741w | 735s | 757s | 752w |
| 1252m | 1250m | 1239w | 1247w | | 707w | 704w | 719sh | 745s | |
| 1217vw | 1217w | 1205m | 1205w | | 617w | | 576s | 547s | 597sd |
| 1163vs | 1163vs | | | | 575sd | 582sd | 560sd | 520s | |

* s = strong, m = medium, w = weak, sh = shoulder, v = very, d = diffuse.

In metal–amine complexes the four principal regions of absorption are ~3300, ~1600, ~1300, and ~800 cm.$^{-1}$. These have been assigned to the NH stretching mode,[1] the asymmetric deformation,[2] the symmetric deformation,[2] and the $NH_3$ rocking mode [2,3] respectively.

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[1] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[2] Mizushima, Nakagawa, and Quagliano, *J. Chem. Phys.*, 1955, **23**, 136.

[3] Barrow, Kreuger, and Basolo, *J. Nucl. Inorg. Chem.*, 1956, **2**, 2340; Sheppard and Powell, *J.*, 1956, 4495, 3108.

TABLE 4. *Frequencies* (*cm.*$^{-1}$) *of the* $NH_2$ *and* $ND_2$ *vibrations in undeuterated and deuterated* $[Co(en)_3]X_3$.

| X = Cl | | | X = SCN | | | X = Cl | | | X = SCN | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D |
| 3215 | 2396 | 1·34 | 3175 | 2381 | 1·36 | 1159 | 962 | 1·21 | 1152 | 961 | 1·20 |
| 3086 | 2288 | 1·35 | 3077 | 2252 | 1·37 | 1125 | 947 | 1·19 | 1129 | 934 | 1·21 |
| 1585 | 1181 | 1·34 | 1582 | 1166 | 1·36 | 1005 | 866 | 1·16 | 1015 | | |
| 1555 | 1152 | 1·35 | 1538 | | | | | | 1005 | 840 | 1·19 |
| | | | | | | 781 | 660 | 1·19 | 800 | 666 | 1·19 |

TABLE 5. *Frequencies* (*cm.*$^{-1}$) *of the* $NH_2$ *and* $ND_2$ *vibrations in undeuterated and deuterated* trans-$[Co(en)_2Cl_2]X$.

| X = Cl | | | X = SCN | | | X = Cl | | | X = SCN | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D | N-H | N-D | N-H/N-D |
| 3250 | 2439 | 1·33 | 3247 | 2445 | 1·33 | 1120 | 961 | 1·17 | 1110 | 950 | 1·18 |
| 3165 | 2410 | 1·31 | 3190 | 2375 | 1·34 | 1110 | 935 | 1·18 | | | |
| 3077 | 2273 | 1·35 | 3120 | 2309 | 1·35 | | | | | | |
| | | | | | | 1004 | 847 | 1·19 | 1008 | 855 | 1·18 |
| 1591 | 1176 | 1·35 | 1585 | 1176 | 1·35 | 994 | 812 | 1·22 | 993 | 821 | 1·21 |
| | | | | | | | | | 798 | 671 | 1·19 |

In the ethylenediamine complexes measured, the main bands in the NH stretching region occur between 3300 and 3077 cm.$^{-1}$ The bands shift on deuteration to 2400—2200 cm.$^{-1}$.

The bands at about 1600 cm.$^{-1}$ may be assigned to the $NH_2$ bending vibration; on deuteration shifts occur to the region 1180—1150 cm.$^{-1}$, in good agreement with the predictions of Mizushima *et al.*[2] for ammine complexes.

The remaining three sets of bands show smaller isotope shifts and can be assigned to vibrations of the $NH_2$ group as a unit, *viz.*, wagging, twisting, and rocking modes respectively.

(b) *Other vibrations of the ethylenediamine-chelate ring.* Quagliano and Mizushima [4] indicated that the cobalt–ethylenediamine ring is in the *gauche*-configuration. The *X*-ray crystallographic data on the compounds *trans*-$[Co(en)_2Cl_2]Cl,HCl,2H_2O$ [5] and trisethylenediaminecobalt chloride [6] support this conclusion. Since the infrared spectra of all the cobalt–ethylenediamine complexes measured show the same general band type, it seems reasonable to assume that all these chelate rings have the *gauche*-configuration. Sheppard and Powell [7] suggested that this general band structure is typical of the *gauche*-configuration of all metal–ethylenediamine rings.

The bands which are unaffected by deuteration and may be assigned to vibrations of the $CH_2$ group, appear in the regions ~1460, ~1300, ~1050, and ~900 cm.$^{-1}$. By comparison with the assignments by Mizushima, Quagliano, and their co-workers [8] for similar five-membered rings of the *gauche*-type, tentative assignments can be made for these bands. Those in the 1460, 1300, and 900 cm.$^{-1}$ regions may be assigned to the $CH_2$ bend, $CH_2$ wag, and the $CH_2$ rock respectively. The band at 1050 cm.$^{-1}$ (which is sharp and strong and appears in all the complexes measured) could be the result of the stretching vibration of either the C–N or the C–C bond.

*Differences in the Spectra of* cis- *and* trans-*Ethylenediamine Complexes.*—The differences in the spectra of the *cis*- and *trans*-complexes of the type $[Co(en)_2Cl_2]X$ in the 1600 cm.$^{-1}$

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[4] Quagliano and Mizushima, *J. Amer. Chem. Soc.*, 1953, **75**, 6084.

[5] Nakahara, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1956, **29**, 428.

[6] Nakatsu, Shiro, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158; Saito, Nakatsu, Shiro, and Kuroya, *Acta Cryst.*, 1955, **25**, 731.

[7] Sheppard and Powell, *J.*, 1959, 791.

[8] Mizushima, Nakagawa, Ichishima, and Quagliano, *J. Phys. Chem.*, 1955, **59**, 293; Lane, Sen, and Quagliano, *J. Chem. Phys.*, 1954, **22**, 1955.

region are in general agreement with those found by Merritt and Wiberly.[9] In the *trans*-bisethylenediamine complexes single sharp bands occur in the range 1605—1575 cm.$^{-1}$, whereas in the *cis*- and trisethylenediamine complexes the band structures are more complex and occur over the wider range 1634—1527 cm.$^{-1}$. Merritt and Wiberly also reported differences between the spectra in the region of the $NH_2$ rocking frequencies. However, hydrogen bonding of the type N–H • • • X has been found to raise these frequencies in metal ammines,[10] and the present work has shown that in a series of compounds of the type $[Co(en)_2AB]X$, the positions and shapes of the bands in this region depend, not only on the geometrical configuration, but also on the nature of the groups A, B, and X.

In this region the *trans*-bisethylenediamine complexes show two sharp bands in the ranges 820—780 cm.$^{-1}$. More complex band structures are found in the *cis*- and tris-complex ions. In general, salts of anions which are able to form hydrogen bonds show higher frequencies and simpler spectra in this region. The spectra of *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ and $[Co(en)_2Cl_2]ClO_4$ are shown in Fig. 1.

FIG. 1. *Infrared absorption spectra from* 10 *to* 18μ *of* (*A*) *cis*-$[Co(en)_2Cl_2]ClO_4$, (*B*) *trans*-$[Co(en)_2Cl_2]ClO_4$, (*C*) *cis*-$[Co(en)_2Cl_2]Cl$, (*D*) *trans*-$[Co(en)_2Cl_2]Cl$.

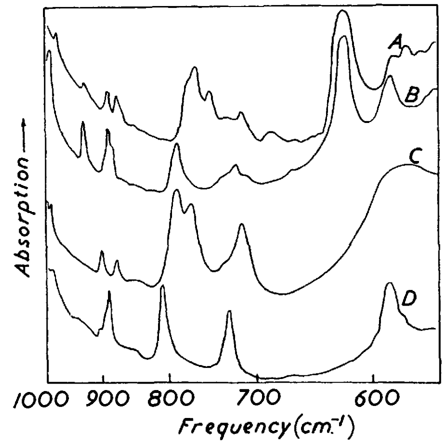
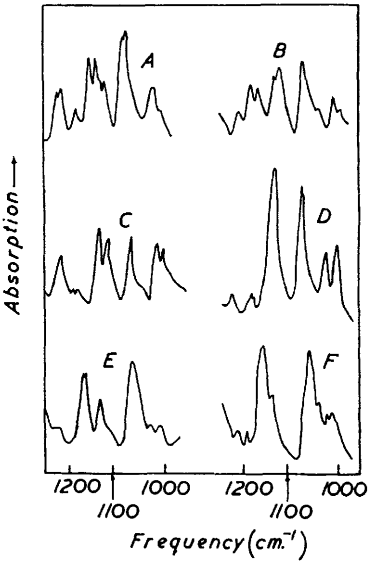


FIG. 2. *Infrared absorption spectra from* 8 *to* 10μ *of* (*A*) *cis*-$[Co(en)_2Cl_2]Cl$, (*B*) *cis*-$[Co(en)_2Cl_2]SCN$, (*C*) *trans*-$[Co(en)_2Cl_2]Cl$, (*D*) *trans*-$[Co(en)_2Cl_2]SCN$, (*E*) $[Co(en)_3]Cl_3$, (*F*) $[Co(en)_3](SCN)_3$.



There are other indications of hydrogen bonding in both the NH stretching and the NH bending regions. In the stretching region the main peaks for *cis*- and *trans*-bisethylenediamine complexes fall between 3289 and 3077 cm.$^{-1}$, and the highest frequencies occur with the salts of less deformable anions, *e.g.*, perchlorate and dithionate, the lowest being for chloride and bromide. The occurrence of three main bands in some complexes can be attributed to the simultaneous vibrations of hydrogen-bonded and free NH groups.[11]

Chamberlain and Bailar[12] suggested that the region 1120—1150 cm.$^{-1}$ can be used to distinguish *cis*- and *trans*-bisethylenediamine isomers. Apart from the obvious disadvantage that this region cannot be used when complexes contain co-ordinated or ionic oxy-anions, the band structures have been found to depend on the anion. In the halide

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[9] Merritt and Wiberley, *J. Phys. Chem.*, 1955, **59**, 55.

[10] Hill and Rosenberg, *J. Chem. Phys.*, 1954, **22**, 148; Fujita, Nakamoto, and Koboyashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 253.

[12] Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412.

ion complexes the *trans*-compounds show two sharp peaks in the ranges 1120—1110 and 1104—1100 cm.$^{-1}$. The cyanate and thiocyanate, however, show only one band at 1110 cm.$^{-1}$. The *cis*-complexes containing halide ions show a group of four bands in this region while the thiocyanates show only two. Trisethylenediamine complexes with halide ions have two distinct bands, at 1163—1150 and 1125—1109 cm.$^{-1}$, while the thiocyanate shows one sharp band, at 1152 cm.$^{-1}$, and a shoulder at 1129 cm.$^{-1}$ (see Fig. 2). Until the effects of hydrogen bonding and ionic interactions on the NH vibrations are elucidated, they can be of little use in distinguishing between the isomers.

The most consistent variations between the spectra of *cis*- and *trans*-isomers have been found in the $CH_2$ rocking region, *i.e.*, 870—900 cm.$^{-1}$. Here complexes with a *cis*-configuration show two bands, while those with a *trans*-structure show one. The positions of the bands in compounds of the type $[Co(en)_2AB]X$ are not dependent on any of the groups A, B, and X, although some splitting may occur in salts of large anions. A large number of salts has been studied in this region, and some of the results are given in Table 6. This region, therefore provides a convenient method for distinguishing between the *cis*- and *trans*-isomers of bisethylenediamine complexes. As two bands are also found in this region in the trisethylenediamine complexes (see Table 3), it seems likely that the splitting occurs when the two ethylenediamine chelate rings are near to each other in space.

TABLE 6. *Frequencies* (*cm.*$^{-1}$) *of absorption bands in the region* 870—900 *cm.*$^{-1}$ *of compounds of the type* $[Co(en)_2AB]X$.

| | A | B | X | *cis* | | *trans* | |
|---|---|---|---|---|---|---|---|
| * | Cl | OH | Cl | 892 | 874 | 893 | |
| | Cl | NCS | SCN | — | — | 885 | |
| | Cl | NCS | $S_2H_6$ | — | — | 889 | |
| | Cl | NCS | $ClO_4$ | 893 | 877 | — | |
| | NCS | NCS | Cl | 891 | 879 | 886 | |
| | NCS | NCS | $NO_2$ | 892 | 883 | 895 | |
| † | $N_3$ | $N_3$ | $ClO_4$ | 892 | 877 | 897 | |
| * | $NH_3$ | $NO_3$ | $S_2O_6$ | 899 | 881 | 887 | 894sh |
| * | $NH_3$ | $NH_3$ | $ClO_4$ | — | — | 895 | 892sh |
| * | $NH_3$ | $OH_2$ | $NO_3$ | — | — | 888 | |
| * | $NH_3$ | Cl | $ClO_4$ | — | — | 888 | |
| | NCS | OH | SCN | — | — | 887 | 895sh |
| * | $NO_2$ | Br | $NO_3$ | — | — | 892 | |
| | $NO_2$ | Cl | Cl | 891 | 879 | — | |
| | $NO_2$ | Cl | SCN | 891 | 878 | — | |
| | $NO_2$ | Cl | $NO_2$ | | | | |
| | NCS | $NO_2$ | Cl | 891 | 880 | — | |
| | NCS | $NO_2$ | SCN | 893 | 877 | — | |
| | NCS | $OH_2$ | $S_2O_6$ | 893 | 877 | — | |
| * | NCS | $NO_2$ | $NO_2$ | 892 | 879 | — | |
| * | $NH_3$ | $OH_2$ | Br | 892 | 881 | — | |
| * | OH | $OH_2$ | $S_2O_6$ | 900 | 885 | — | |

* The author thanks Dr. M. L. Tobe for samples of these compounds. † The author thanks Dr. P. J. Staples for samples of these compounds.

*Configuration of the Individual Chelate Rings.*—It has been pointed out by Bailar and Corey [13] that an isolated metal–ethylenediamine ring in the *gauche*-form can adopt either of two configurations (*k* and *k*′) which are energetically and geometrically equivalent, but are enantiomeric. A compound having more than one ethylenediamine ring, even for fixed positions of the donor nitrogen atoms, may then have rings with either the *k*- or the *k*′-configuration. Although the energy of conversion is expected to be small, the compounds containing different ring forms will differ slightly in thermodynamic stability. By considering the non-bonded interactions of the donor nitrogen groups, Corey and Bailar estimated that for the *trans*-bisethylenediamine arrangement, the *kk*-form is more stable. However, *X*-ray data indicate that in the solid state the two rings are in mirror image forms (*kk*′-form). Fig. 3 shows that in the *kk*′-form, the hydrogen atoms attached

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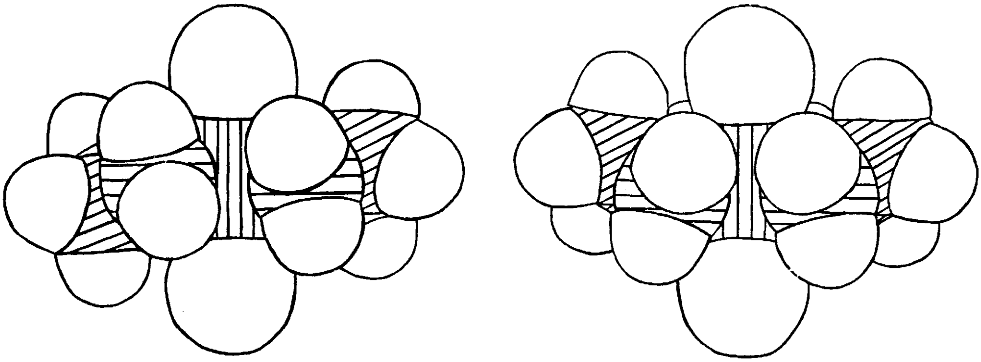
[13] Bailar and Corey, *J. Amer. Chem. Soc.*, 1959, **81**, 2623.

to the donor nitrogen atoms, although giving greater hydrogen–hydrogen interactions, are in a favourable position for hydrogen bonding with the anion.

It appears possible that in the solid state the *kk'*-form of the *trans*-bisethylenediamine complex is stabilised by interaction with the anion. The compounds that show the greatest amount of hydrogen bonding as assessed from the $NH_2$ frequencies also give the simplest spectra. Compounds that are not fixed by specific interaction should contain both the *kk*- and the *kk'*-form, thus producing a greater complexity of band structure because of the lower symmetry of the *kk*-form.

FIG. 3. *trans*-$[Co(en)_2Cl_2]^+$: (*a*) *kk-form,* (*b*) *kk'-form.*



(*a*) (*b*)

## EXPERIMENTAL

*Determination of Spectra.*—The spectra were recorded on a Grubb–Parson G.S. 2A double-beam spectrometer. Solid samples in Nujol (B.P. grade) mulls were examined between rock-salt plates.

*Anion Analysis.*—A known weight of the complex was passed through a column of Amberlite IR-120 resin in the acid form. The equivalent of acid in the effluent was titrated with standard borax, Bromophenol Blue being used as indicator.

*Preparation of Compounds.*—trans-*Dichlorobisethylenediaminecobalt*(III) *salts.* (*a*) Chloride. *trans*-$[Co(en)_2Cl_2]Cl$ was prepared by Bailar's method [14] and recrystallised from warm water (Found: $Cl^-$, 12·4. Calc. for $C_4H_{16}N_4Cl_2CoCl$: $Cl^-$, 12·4%).

(*b*) Bromide. This was prepared by Jörgensen's method [15] (Found: $Br^-$, 23·9. Calc. for $C_4H_{16}N_4Cl_2BrCo$: $Br^-$, 24·2%).

(*c*) Iodide. This was prepared by the same author's method (Found: $I^-$, 34·0. Calc. for $C_4H_{16}N_4Cl_2ICo$: $I^-$, 33·7%).

(*d*) Thiocyanate. This was prepared by adding a solution of sodium thiocyanate to a solution of the chloride of the series [Found: $SCN^-$, 18·3. Calc. for $C_4H_{16}N_4Cl_2Co(SCN)$: $SCN^-$, 18·9%].

(*e*) Perchlorate. The dihydrate was prepared by adding a solution of sodium perchlorate to a solution of the chloride [Found: $ClO_4^-$, 28·1. Calc. for $C_4H_{20}N_4Cl_2O_2Co(ClO_4)$: $ClO_4$, 28·2%].

(*f*) Cyanate. This *salt* was prepared by adding a solution of potassium cyanate to an ice-cold solution of the chloride (Found: C, 20·8; H, 5·8. $C_5H_{16}N_5Cl_2OCo$ requires C, 20·6; H, 5·6%). The *cis*-isomer was not isolated.

(*g*) Nitrate. The dihydrate was prepared by adding a solution of sodium nitrate to one of the chloride [Found: $NO_3^-$, 17·7. Calc. for $C_4H_{20}N_4Cl_2O_2Co(NO_3)$: $NO_3^-$, 17·9%].

(*h*) For the *dithionate* Jörgensen's method [15] was used [Found: $S_2O_6^{2-}$, 24·3. Calc. for $(C_4H_{16}N_4Cl_2Co)_2S_2O_6$: $S_2O_6^{2-}$, 24·3%].

cis-*Dichlorobisethylenediaminecobalt*(III) *salts.* (*a*) Chloride. *cis*-$[Co(en)_2Cl_2]Cl,H_2O$ was prepared by Bailar's method [14] (Found: $Cl^-$, 11·6. Calc. for $C_4H_{18}N_4Cl_2OCo$: $Cl^-$, 11·7%).

[14] Bailar, " Inorganic Syntheses," McGraw-Hill, New York, 1946, Vol. II, p. 223.

[15] Jörgensen, *J. prakt. Chem.*, 1890, **41**, 441, 453.

(*b*) Bromide. The monohydrate was prepared from a solution of the chloride by addition of hydrobromic acid (Found: $Br^-$, 23·0. Calc. for $C_4H_{18}N_4Cl_2OBrCo$: $Br^-$, 23·0%).

(*c*) Iodide. Werner's method [16] was used (Found: $I^-$, 33·5. Calc. for $C_4H_{16}N_4Cl_2ICo$: $I^-$, 33·7%).

(*d*) Thiocyanate. This was prepared by addition of sodium thiocyanate to a solution of the chloride (Found: $SCN^-$, 19·1. Calc. for $C_4H_{16}N_4Cl_2CoSCN$: $SCN^-$, 18·9%).

(*e*) Perchlorate. The dihydrate was prepared from the chloride by addition of aqueous sodium perchlorate (Found: $ClO_4^-$, 27·8. Calc. for $C_4H_{20}N_4Cl_2O_2CoClO_4$: $ClO_4^-$, 28·2%).

(*f*) Dithionate. This was prepared from the chloride by addition of aqueous sodium dithionate [Found: $S_2O_6^{2-}$, 24·3. Calc. for $(C_4H_{16}N_4Cl_2Co)_2S_2O_6$: $S_2O_6^{2-}$, 26·8%].

*Trisethylenediaminecobalt*(III) *salts.* (*a*) The chloride, $[Co(en)_3]Cl_3,3H_2O$, was prepared by Work's method [17] (Found: $Cl^-$, 27·2. Calc. for $C_6H_{30}N_6Cl_3O_3Co$: $Cl^-$, 26·8%).

(*b*) Bromide. The trihydrate was prepared by addition of hydrobromic acid to the chloride (Found: $Br^-$, 45·1. Calc. for $C_6H_{30}N_6Br_3O_3Co$: $Br^-$, 45·0%).

(*c*) Iodide. The monohydrate was prepared from the bromide by the action of potassium iodide (Found: $I^-$, 59·4. Calc. for $C_6H_{26}N_6I_3OCo$: $I^-$, 59·8%).

(*d*) Thiocyanate. This was precipitated by addition of sodium thiocyanate to a solution of the chloride (Found: $SCN^-$, 41·7. Calc. for $C_6H_{24}N_6CoS_3C_3N_3$: $SCN^-$, 42·1%).

(*e*) Perchlorate. This was prepared from the chloride by addition of aqueous sodium perchlorate (Found: $ClO_4^-$, 55·3. Calc. for $C_6H_{24}N_6CoCl_3O_{12}$: $ClO_4^-$, 55·7%).

*Chloroisothiocyanatobisethylenediamine salts.* (*a*) *trans*-Thiocyanate. This was prepared from *trans*-$[Co(en)_2Cl_2]Cl$ and potassium thiocyanate by Werner's method [16] (Found: $SCN^-$, 17·0. Calc. for $C_5H_{16}N_5SClCoSCN$: $SCN^-$, 17·6%).

(*b*) *trans*-Dithionate. This was prepared by Werner's method [16] [Found: $S_2O_6^{2-}$, 22·2. Calc. for $(C_5H_{16}N_5SClCo)_2S_2O_6$: $S_2O_6^{2-}$, 22·7%].

(*c*) *cis*-Chloride. Werner's method [16] was used (Found: Co, 19·35. Calc. for $C_5H_{16}N_5SCl_2Co$: Co, 19·2%).

(*d*) *cis*-Perchlorate. The monohydrate was prepared by the action of perchloric acid on the *cis*-chloride (Found: C, 15·45; H, 4·6. Calc. for $C_5H_{18}N_5SCl_2O_5Co$: C, 15·4; H, 4·6%).

*Chloronitrobisethylenediamine salts.* (*a*) *cis*-Chloride. *cis*-$[Co(en)_2ClNO_2]Cl$ was prepared by the action of sodium nitrite on *trans*-$[Co(en)_2Cl_2]Cl$ according to Werner [16] (Found: $Cl^-$, 11·6. Calc. for $C_4H_{16}N_5O_2ClCoCl$: $Cl^-$, 11·9%).

(*b*) *cis*-Thiocyanate. This was prepared by the action of aqueous potassium thiocyanate on the chloride (Found: $SCN^-$, 18·4. Calc. for $C_4H_{16}N_5O_2ClCoSCN$: $SCN^-$, 18·6%).

(*c*) *cis*-Nitrite. Werner and Gerb's method [18] was used (Found: C, 15·2; H, 5·1. Calc. for $C_4H_{16}N_7O_4ClCo$: C, 15·65; H, 5·2%).

*Nitroisothiocyanatobisethylenediamine salts.* (*a*) *cis*-Chloride. Prepared by Werner's method [16] (Found: $Cl^-$, 12·3. Calc. for $C_5H_{16}N_6SO_2CoCl$: $Cl^-$, 12·3%).

(*b*) *cis*-Thiocyanate. This was prepared from the chloride by addition of aqueous potassium thiocyanate (Found: $SCN^-$, 16·8. Calc. for $C_5H_{16}N_6SO_2CoSCN$: $SCN^-$, 17·1%).

*Di-isothiocyanatobisethylenediamine salts.* (*a*) *cis*-Chloride. The monohydrate was prepared by Werner's method [16] (Found: C, 21·2; H, 5·1. Calc. for $C_6H_{18}N_6S_2OClCo$: C, 20·7; H, 5·2%).

(*b*) *cis*-Nitrite. The monohydrate was obtained by addition of sodium nitrite to the chloride (Found: C, 20·5; H, 5·4. Calc. for $C_6H_{18}N_7S_2O_3Co$: C, 20·1; H, 5·1%).

(*c*) *trans*-Chloride. This was prepared as monohydrate by the action of hydrochloric acid on the thiocyanate (Found: C, 21·0; H, 5·7. Calc. for $C_6H_{18}N_6S_2OClCo$: C, 20·7; H, 5·2%).

(*d*) *trans*-Nitrite. This was prepared by the action of sodium nitrite on the chloride (Found: C, 22·4; H, 4·9. Calc. for $C_6H_{16}N_7S_2O_2Co$: C, 21·2; H, 4·9%).

trans-*Isothiocyanatohydroxobisethylenediaminecobalt*(III) *thiocyanate.* The monohydrate was prepared by Werner's method [16] (Found: C, 21·9; H, 6·3; Co, 17·7. Calc. for $C_6H_{19}N_6S_2O_2Co$: C, 21·9; H, 5·8; Co, 17·8%).

cis-*Isothiocyanatoaquobisethylenediaminecobalt*(III) *dithionate.* The trihydrate was prepared by passing *cis*-$[Co(en)_2NCSCl]Cl$ through a column of Amberlite IR-400 resin in the hydroxide form and neutralising the effluent with dithionic acid, which had been prepared by passing

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[16] Werner, *Annalen*, 1912, **386**, 1.

[17] Work, ref. 14, p. 221.

[18] Werner and Gerb, *Ber.*, 1901, **34**, 1742.

sodium dithionate through a column of Amberlite IR-120 resin in the acid form. The complex dithionate was precipitated by addition of alcohol (Found: Co, 12·5. Calc. for $C_4H_{24}N_4O_{10}S_2Co$: Co, 12·5%).

*Deuterated Compounds.*—In alkaline solution, the hydrogen atoms attached to the donor nitrogen atoms, as with the ammino-complexes,[19] undergo exchange with the solvent. Deuterated trisethylenediaminecobalt(III) chloride was prepared from the protonated complex. $[Co(en)_3]Cl_3$ was dissolved in 99·80% deuterium oxide made approximately M in hydroxide (~0·04 g. of sodium hydroxide in 1 ml. of deuterium oxide) and the mixture was stored at 40° for 30 min. The deuterated chloride was precipitated by addition of concentrated hydrochloric acid after the mixture had been cooled to 10°. The analysis fits a *compound* containing three molecules of deuterium oxide of crystallisation, *i.e.*, $[Co(ND_2{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_3]Cl_3,3D_2O$ (Found: C, 17·2; H + D, 10·0. $C_6H_{12}D_{18}N_6O_3Co$ requires C, 17·2; H + D, 10·5%).

The thiocyanate was prepared from the chloride by addition of aqueous sodium thiocyanate. The analysis indicates that the *compound* has one molecule of deuterium oxide of crystallisation, *i.e.*, $[Co(ND_2{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_3](SCN)_3,D_2O$. The protonated compound is anhydrous. Bands observed in the D–O stretching region in the infrared spectrum also show the presence of deuterium oxide (Found: C, 24·2; H + D, 9·1. $C_9H_{12}D_{14}N_9S_3OCo$ requires C, 24·3; H + D, 9·0%).

Deuterated *trans*-dichlorobisethylenediaminecobalt(III) salts were prepared from *trans*-$[Co(en)_2Cl_2]Cl$. The protonated chloride was dissolved in 99·80% $D_2O$ (1M with respect to hydroxide), and the mixture left overnight. Excess of concentrated hydrochloric acid was added, and the mixture heated to dryness on a water-bath. The resulting green crystals were dried at 110°. A sample of the deuterated chloride was taken for infrared analysis. A solution of sodium thiocyanate was added to the rest, and the deuterated *thiocyanate* was precipitated (Found: $SCN^-$, 17·3. $C_5H_8D_8N_5SCl_2Co$ requires $SCN^-$, 17·6%).

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[19] Anderson, Spoor, and Briscoe, *J.*, 1943, 361; Brock and Gold, *J.*, 1959, 966.