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Studies of 8-Mercaptoquinoline as Chelate Agents. II. Infrared Absorption Spectra of its Divalent Metal Chelates

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The infrared spectra of divalent metal thiooxinates have been measured in the region between 4000 and 400 cm^{-1}, and the relationships between these spectral bands and the characteristics of the metal-ligand bonding and the structures of the thiooxinates have been discussed. The plots of the frequencies of the metal-sensitive bands around 990 and 670 cm^{-1} against the atomic weight of the metal make it possible to classify these metal thiooxinates into two groups, one of which includes Cu-, Co-, Ni-, and Mn-thiooxinate, and the other, Cd-, Zn-, and Pb-thiooxinate. The deviation of the point for Zn-thiooxinate from the line belonging to thiooxinates with such metal atoms as have no available *d*-orbitals has been compared with the case of oxinates. Moreover, from the appearance of the 450 cm^{-1} band in the latter group, the structure of these thiooxinates may be tetrahedral. As for the frequencies of the two metal-sensitive bands mentioned above, those of Pd- and Pt-thiooxinate are the highest and that of Ag(I)-thiooxinate, examined for the sake of comparison, is the lowest. The possibility of the analytical application of the metal-sensitive band around 670 cm^{-1} has been discussed.

In the previous paper[1] describing infrared studies of 8-mercaptoquinoline, it was suggested that some substituent-sensitive bands are affected by the mass of the substituent atom directly bonded to the ring, and that these bands may be regarded as metal-sensitive bands (the 9μ band of metal oxinates,[2] for example, can be used for an analysis using infrared spectrometry).

Although several references concerning infrared studies of metal oxinates have been reported,[2-6] studies of the infrared spectra of the metal chelates of thiooxine with sulfur and nitrogen atoms as ligands have been limited in number.

From the investigations of the acid dissociation phenomena of oxine (HQ), thiooxine (MQ), and selenooxine (SeQ), HQ would be expected to yield a significantly more stable 1 : 1 metal chelate than MQ and SeQ, but this is not true. This has been interpreted as resulting from the greater covalent characteristic of the metal-ligand bond for thiooxinate and selenooxinate than in that for oxinate and from the possibility of π-bonding between the metal and ligand atoms for thiooxinate[7] or selenooxinate.[8]

In order to elucidate the relationships among some infrared bands, the character of the metal chelate-bonding, and the structure of thiooxinates, the infrared spectra of divalent metal chelates of MQ were studied.

Experimental

Reagents. The sodium salt of MQ was prepared by the method described in the previous paper.[1] The other reagents of an analytical grade were used without further purification.

Metal Thiooxinates. Divalent metal chelates of MQ were prepared under nitrogen gas and were purified by a technique developed from Dalziel-Kealey's method.[9] The

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[1] Y. Mido and E. Sekido, This Bulletin, **44**, 2127 (1971).

[2] R. G. Charles, H. Freiser, R. Freidel, L. E. Hillard, and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

[3] K. G. Stone, *J. Amer. Chem. Soc.*, **76**, 792 (1954).

[4] J. E. Tachett and D. T. Sawyer, *Inorg. Chem.*, **5**, 692 (1964).

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[6] J. C. Fanning and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, **25**, 29 (1963).

[7] A. Corsini, Q. Fernando, and H. Freiser, *Anal. Chem.*, **35**, 1424 (1963).

[8] E. Sekido, Q. Fernando, and H. Freiser, *Anal. Chem.*, **36**, 1768 (1964); *ibid.*, **37**, 1556 (1965).

[9] J. A. W. Dalziel and D. Kealey, *Analyst*, **89**, 411 (1964).

TABLE 1. ANALYTICAL DATA FOR VARIOUS METAL THIOOXINATES

Formula	Color	Analysis % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N	pH for ppt.
$Mn(C_9H_6NS)_2$	yellow ochre	57.59	3.22	7.46	55.72	3.26	6.68	4.5
$Co(C_9H_6NS)_2$	brown	56.99	3.19	7.38	53.30	3.00	6.79	4.5
$Ni(C_9H_6NS)_2$	dark magenta	57.02	3.19	7.39	57.39	3.49	7.38	4.5
$Cu(C_9H_6NS)_2$	brown	56.31	3.15	7.29	56.17	3.35	7.40	4.5
$Zn(C_9H_6NS)_2$	bright yellow	56.04	3.14	7.26	56.12	3.16	7.42	4.5
$Cd(C_9H_6NS)_2$	chrome yellow	49.95	2.80	6.47	49.64	2.61	6.52	4.5
$Pb(C_9H_6NS)_2$	chrome yellow	40.98	2.29	5.31	41.29	2.51	5.60	5.5
$Pd(C_9H_6NS)_2$	brick reddish black	50.65	2.83	—	50.60	3.13	—	3.0
$Pt(C_9H_6NS)_2$	brown	41.94	2.35	—	41.59	2.86	—	10.0
$Ag(C_9H_6NS)$	chrome yellow	40.32	2.26	—	40.12	2.67	—	9.5

All of the metal thiooxinates were dryed at 120°C for several hours.

results of the elementary analysis of these metal chelates are summarized in Table 1. The results for Mn- and Co-thiooxinate are slightly different from those expected for each proposed formula.

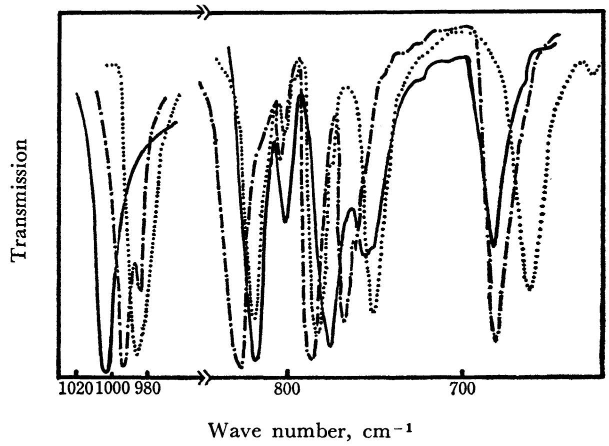
Infrared Spectra. The infrared spectra were measured in the region between 4000 and 400 cm^{-1} with a Hitachi EPI-2G Infrared Grating Spectrophotometer. The spectrometer was calibrated with standard polystyrene film and water vapor. In the measurement, both the potassium bromide disc- and Nujol mulls-method were usually used, and both gave the same infrared spectra. To obtain a high resolution, the spectra in the special region where significant bands exist were repeatedly recorded at a slow speed and using a five-fold-scale expansion. The recorded spectra should be accurate to within ±1 cm^{-1}.

Results and Discussion

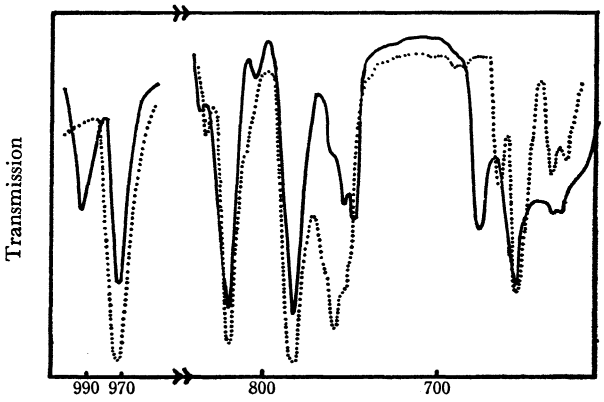
The absorption frequencies of some divalent metal thiooxinates are summarized in Table 2. The spectra of the metal thiooxinates are all essentially similar to each other and to those of anhydride(liquid),[10] the disulfide and sodium salt of MQ which have been reported previously.[1]

Metal-Sensitive Bands and Structures of Metal Thiooxinates. Metal thiooxinates show a relatively strong absorption band in *the 1011—986 cm^{-1} region* and another strong band in *the 693—662 cm^{-1} region,* as shown in Table 2 and in Fig. 1. These bands have been assigned to substituent-sensitive bands.[1]

Although these thiooxinates show a few weak bands on the lower-frequency side of the metal-sensitive bands, it may be concluded, on the basis of an examination of the corresponding bands in each region of the disulfide of MQ (973 and 655 cm^{-1}), that all these thiooxinates are regular chelates except Mn-thiooxinate. For Mn-thiooxinate, as is shown in Fig. 1-(b), each metal-sensitive band appears as two bands, at 994 and 974 cm^{-1} (for *the 990 cm^{-1} band*) and at 674 and 655 cm^{-1} (for *the 670 cm^{-1} band*) respectively, and each latter band can be superimposed upon the corresponding bands of the disulfide of MQ. This suggests that these bands at 994 and 674 cm^{-1} may also be attributable to the metal-sensitive bands of a regular Mn-thiooxinate in a probable mixture with the disulfide of MQ and/or another chelate.



(a) ——: Cu-thiooxinate, ·—·: Zn-thiooxinate, ······: Ag(I)-thiooxinate



(b) ——: Mn-thiooxinate, ······: Disulfide of MQ

Fig. 1. Infrared spectra of some metal thiooxinates.

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[10] The absence of ν_{SH}(2515 cm^{-1}) in this spectrum may show the formation of metal chelate.

TABLE 2. OBSERVED FREQUENCIES (IN cm^{-1}) OF DIVALENT METAL CHELATES OF 8-MERCAPTOQUINOLINE[a, b)]

Mn	Co	Ni	Cu	Zn	Cd	Pb	Pd	Pt	Ag(I)
1600 m	1655 w			1595 w	1598 w	1594 w	1613 w	1597 w	1598 w
1590 m	1580 s	1587 m	1580 w	1585 w	1582 m	1584 w	1589 w	1583 w	1586 w
1555 vw	1553 m	1560 vw	1553 vw	1566 w	1553 vw	1554 w	1560 w	1558 m	1552 m
1489 s	1490 s	1491 s	1492 s	1489 s	1492 s	1494 s	1496 s	1498 s	1492 s
1449 m	1447 s	1448 m	1450 m	1449 1443 s	1446 s	1448 s	1452 s	1453 s	1449 s
1415 vw	1411 w	1416 w		1413 w	1410 vw	1413 w	1417 w	1417 w	1416 w
1380 w	1372 m	1375 w	1376 m	1371 s	1377 m	1380 1372 m	1384 m	1376 s	1377 s
1360 s	1360 s	1362 s	1360 s	1365 s	1360 s	1360 s	1363 s	1364 s	1356 s
1300 s	1299 s	1303 s	1300 s	1300 s	1300 s	1300 s	1303 m	1302 m	1297 s
1233 vw		1238 w	1235 vw	1235 m	1237 w	1234 m	1233 w		1232 w
1211 m	1211 s	1213 s	1209 s	1217 s	1212 s	1212 s	1215 m	1211 s	1211 s
1130 w	1134 w	1140 w	1130 vw	1129 w	1129 w	1134 w	1133 w	1136 w	1131 w
1060 m	1061 w	1072 w	1070 w	1069 w	1064 m	1070 w	1071 w	1081 w	1067 m
1028 vw	1044 w	1045 w	1043 vw	1045 w	1040 w	1040 w	1051 m	1065 m 1054 w	1034 w
994 w	996 s	997 s	1002 s	994 s[d)] 985 m	988 s	989 s	1008 s	1011 s	986 s
974 s[c)]	974 s[c)]	973 m	975 w		975 w			974 w	
	954 w	956 w	947 vw	954 vw	955 vw	940 vw	960 vw		950 vw
894 vw	880 vw	880 w	874 vw	886 vw	882 vw	880 vw	881 vw	870 vw	890 vw
852 vw	864 w	854 w		857 vw	848 w	844 vw	856 w		841 w
833 w 820 s	824 s	818 s	817 s	826 s	819 s	819 s	813 s	811 s	819 s
805 w	803 w	806 w	807 w	805 w	805 w	803 w	801 w	803 w	803 w
782 s	777 s	778 s	776 s	786 s	778 s	781 s	764 s	761 s	782 s
760 w[c)] 753 m 748 m	748 s	748 s	744 s	767 s 761 sh	746 s	754 m 750 m	739 s	740 s	751 m
674 m	675 s	677 s	683 s	682 s	672 s	670 s	692 s	693 m	662 s
655 s[c)]	655 m								
633 626 m[c)]	632 w	634 w	625 w	629 vw	630 w	625 w	613 w	610 w	624 w
	552 w	554 vw	554 vw	555 w	548 vw	547 vw	548 m	553 m	550 w
530 m	530 w	530 w	528 vw	534 w	527 vw	529 vw	530 w	524 w	526 w
	480	470 vw		470 vw					
	446 vw	456 vw	454 vw	454 s	443 m	440 m	444 vw	451 vw	444 vw
436 w	425 w	433 w			420 vw	420 vw	416 w	419 w	

a) Bands in the region between 4000 and 1700 cm^{-1}, where only a kind of fundamental bands ν(C–H) appear 2980 cm^{-1}, were not exhibited in this Table.

b) Abbreviation; w, weak; m, medium; s, strong; v, very strong.

c) *Cf.* Bands of its disulfide, 973(s), 833(w), 760(s), 755(sh), 655(s), 634(w), 626(w) see Fig. 1-(b).

d) A point of Zn* shown in Fig. 2. exhibits the average frequency of bands at 994 and 985 cm^{-1} for Zn-thiooxinate.

Because the results of the elementary analysis of Co-thiooxinate were also slightly different from the expected value for the proposed formula, the infrared spectrum of Co-thiooxinate was compared with that of Co(III)-thiooxinate prepared from the salt of Co (III). The comparison suggests that the Co-thiooxinate formed by a conventional method may be thiooxinate of the divalent cobalt and that the strong bands at 996 and 683 cm^{-1} may be assigned to the metal-sensitive bands for a regular divalent chelate. A more detailed discussion of Co-thiooxinate will be presented in the future.

Charles *et al.*[2)] have examined the infrared spectra of a series of divalent metal oxinates. They described how, when the frequencies of the 9 μ peak associated with a C–O vibration are plotted against the mass of the corresponding metal, the points for the transition metal chelates nearly fall on a straight line (the frequencies increase remarkably as the mass of the metal increases), while the points for the remaining metal chelates fall near on another (the frequencies decrease slowly). They have suggested that this may indicate either the involvement of 3*d*-orbitals in the metal-ligand bonding for the transition metal oxinates or, alternatively, a difference in crystal structure for the two classes of chelates.

In this work, the plot of frequency of *the 990 cm^{-1} band* for thiooxinates is similar to that of the 9 μ band

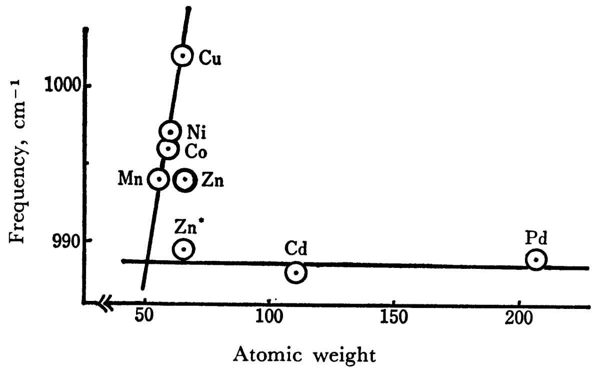

Fig. 2. Relationships between frequency of *the 990 cm*$^{-1}$ *band* and atomic weight of central metal for divalent metal thiooxinate.

* A point of Zn* exhibits the average frequency of bands at 994 and 985 cm^{-1} for Zn-thiooxinate.

in oxinates, as is shown in Fig. 2. The character of this band may be not so simple as the diatomic vibration of oxinates, since the spectral shift is too little considering the large change in atomic weight upon the substitution of sulfur for oxygen as the coordinating atom. A similar plot of *the 670 cm*$^{-1}$ *band* for thiooxinates is shown in Fig. 3. The similarity between these plots of *the 990 and 670 cm*$^{-1}$ *bands* and the Charles plot supports their suggestion. Compared with the case of oxinates, the point for Zn-thiooxinate deviates considerably upwards from the lines belonging to thiooxinates with such metal atoms as have no available *d*-orbitals; the deviation from the line for the *670 cm*$^{-1}$ *band* is larger than that for *the 990 cm*$^{-1}$ *band.*

If the frequencies of *990 cm*$^{-1}$ *bands* are arranged according to wave number, the order is as follows:

Cu->Ni->Co->Zn-=Mn->Pb->Cd-thiooxinate

This order is almost the same as that of the 9 μ band for metal oxinates²⁾ and also that of the 1250 cm^{-1} band for metal 2-(*o*-hydroxyphenyl)-benzoles,¹¹⁾ which chelates through oxygen and nitrogen stoms. In the order of the frequencies for *the 670 cm*$^{-1}$ *band* of thiooxinates, only the Zn-thiooxinate is located between Cu- and Ni-thiooxinate:

Cu->Zn->Ni->Co->Mn->Cd->Pb-thiooxinate

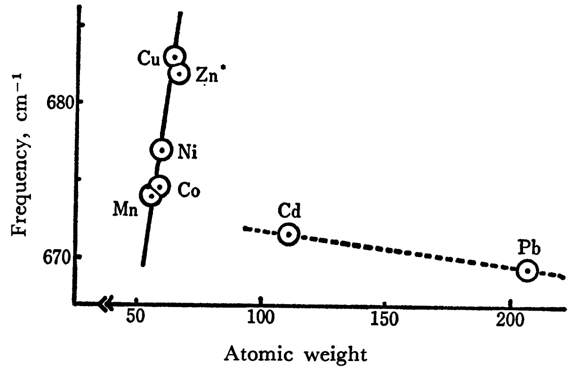

Fig. 3. Relationships between frequency of *the 670 cm*$^{-1}$ *band* and atomic weight of central metal for divalent metal thiooxinate.

In metal selenooxinates, the bands around 975 and 660 cm^{-1} are metal-sensitive;¹²⁾ also the frequencies of both the bands are arranged in the same order as with *the 670 cm*$^{-1}$ *band* for metal thiooxinates.

These facts may suggest that Zn-thiooxinate has a greater covalent character in metal-ligand bonding than does Zn-oxinate, and that the chemical affinity between the sulfur atom and the zinc ion is stronger than that between the oxygen atom and the cation.

A Peak near 450 cm^{-1} *and the Structures of Metal Thiooxinates.* A peak near 450 cm^{-1} appears in Zn-, Cd-, and Pb-thiooxinate, weakenning in relative strength in this order. In the transition-metal thiooxinates, this peak appears only slightly or not at all. Since the transition metal ions have *d*-orbitals available for *dsp*² bonding, it is reasonable to assume that they form square-planar complexes with MQ.

The method of group theory shows that the species of normal modes resulting from the D_{2h}-symmetry of the *trans* square-planar type include A_g, B_g, A_u, and B_u, of which the A_u and B_u species are active in the infrared. The 450 cm^{-1} band may be derived from one of the vibrations corresponding to A_g and B_g species from this type.

Therefore, it may be suggested that the degree of deviation from the square-planar structure is indicated by the effect on the strength of the 450 cm^{-1} band, and that Zn-thiooxinate, which has the largest strength, has a structure nearer to tetrahedral.

This consideration from the selection rule is conclusively supported by the X-ray diffraction studies confirming that Pb-thiooxinate is a distorted tetragonal pyramid¹³⁾ and suggesting that Zn-thiooxinate may be a tetrahedron.¹⁴⁾

C–H Out-of-plane Bending Vibrations. All of the metal thiooxinates exhibit three strong bands assignable to C–H out-of-plane bending vibrations over the range between 820 and 740 cm^{-1}. Although the lowest band is most sensitive to metal, the relationship between its frequency and the atomic weight of the metal is not consistent. The lowest band for Zn- or Pb-thiooxinate splits into two bands; this may be additional evidence in favor of the structural consideration to be expected from the selection rule.

Pt-, Pd-, and Ag(I)-Thiooxinate. In general, the metal-ligand bonding in platinium or palladium chelates is strong covalent, and these chelates are both square planar.¹⁵⁾ The order of the frequencies of the metal-sensitive bands of both the thiooxinates precedes the order presented previously:

Pt->Pd->Cu-thiooxinate······

Also, the metal-sensitive bands of Ag(I)-thiooxinate, examined in order to compare them with divalent metal thiooxinate, appear at 986 and 662 cm^{-1}, and the frequencies of these bands are lower than those of

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11) T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, *J. Amer. Chem. Soc.*. **78**, 260 (1956).

12) This will be discussed in a separate paper.

13) E. A. Shuga, V. M. Agre, J. A. Bankovskis, and E. Luksa, *Zn. Strukt. Khim.*, **8**, 171 (1967); *Chem. Abstr.*, **67**, 6480 m (1967).

14) J. A. Bankovskis, A. Ievins, A. Lokenbakh, and D. Zaruma, *Chem. Abstr.*, **54**, 18151i (1960).

15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York (1963) p. 141.

divalent-metal thiooxinates.

Possibility of Analytical Applications. Although there is considerable similarity among the infrared spectra of metal thiooxinates, each spectrum exhibits a few characteristic bands, as has been mentioned above. Of these bands, *the 670 cm^{-1} band* has more analytical advantages: (1) There is enough apparent difference in the frequency to permit its use in the detection of two metal cations by means of a certain combination of metal cations. (2) There are no near bands affecting this band. (3) The relative intensity of this band is strong.

Pd-thiooxinate was selected as a reference on the basis of the following reasons; (1) the frequency of this band of Pd-thiooxinate is higher than that of any other metal thiooxinate, and (2) this chelate precipitates as a regular chelate over a wide range of pH.[16]

At the optimum pH for the formation of the other metal chelate, sodium salt of MQ reacts with a solution containing the palladium ion and the other metal ion to precipitate a mixture of the two metal chelates. In all these binary systems except the Pd–Pt system, the absorption bands of this mixture can be resolved into two components without any mutual interference; one is of Pd-thiooxinate, while the other is of the other metal thiooxinate.

The infrared spectra of both the Co–Ag and Cu–Ag systems indicated two distinguishable bands. The smallest difference in the frequency between two such bands observed in this binary systems was the 13 cm^{-1} obtained in the Co–Ag system. Therefore, if there is such a degree of difference at least, the metal cations can be identified by infrared study.

To obtain possible quantitative aspects, a typical calibration curve was drawn for Pd-thiooxinate employing the potassium bromide disc method.[5] As is shown in Fig. 4, Beer's law is followed in the 0.6—2.7 mg range of Pd-thiooxinate (0.15—1.11 mg of palladium) for the 300 mg disc.

As an example of a binary system, the Pd–Ni system is presented in Fig. 5. The nickel ion was undetectable in the precipitate from a mixture in which the gram-ionic ratio of the palladium ion to the nickel ion was 5 : 1, but when the ratio was reversed the palladium ion was detectable. This fact may explain why the molar extinction coefficient for this band of Pd-thiooxinate is larger than that of Ni-thiooxinate.

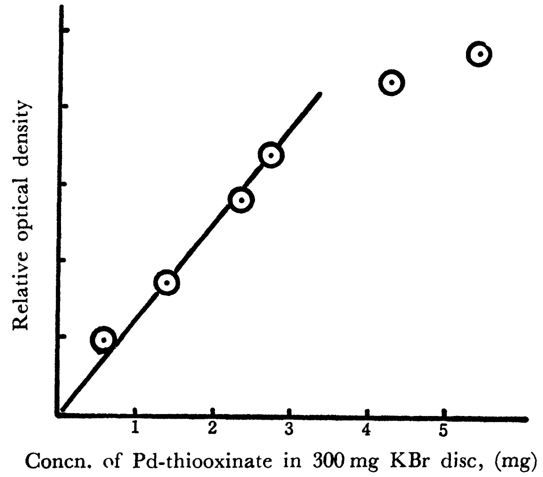

Fig. 4. Calibration curve.

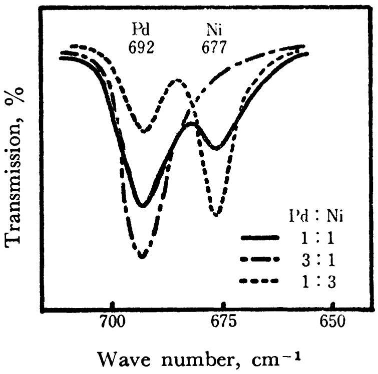

Fig. 5. Infrared spectra of *the 670 cm^{-1} bands* in Pd-Ni system.

Analytical applications of infrared study to metal chelates may be expected to be very useful in the identification of metal thiooxinates, but the other advantage, in quantitative aspects, remains obscure. Some probable disadvantages may be the troublesome for potassium bromide disc preparation and the need for compensation between the relative opitical density and the weight of the dics.

The authors wish to express their thanks to Mr. I. Fujiwara for his assistance in synthesising and to the Ministry of Education for a grant-in-aid.

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[16] Yu. A. Bonkovsky, J. Cirule, and A. Ievins, *Zh. Anal. Khim.*, **13**, 507 (1958).