Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Fernando, Quintus(1966) 'Adduct Formation with Metal Chelates Involved in Liquid-Liquid Extraction', Separation Science and Technology, 1: 5, 575 — 594
To link to this Article: DOI: 10.1080/01496396608049466
URL: http://dx.doi.org/10.1080/01496396608049466

SEPARATION SCIENCE, 1(5), 575–594 (1966)

Adduct Formation with Metal Chelates Involved in Liquid-Liquid Extraction*

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Summary

The factors that influence the formation of metal chelate adducts which are of importance in liquid-liquid extraction are evaluated and correlations between the structures and properties of these adducts discussed. A scheme for the classification of metal chelate adducts is suggested on the basis of available experimental data.

In a study of the donor properties of a series of heterocyclic bases, alkylamines, and alkylphosphines, the square-planar tetracoordinated nickel(II) chelate, diacetylbisbenzoylhydrazino nickel(II), was used as a reference acceptor molecule. This chelate was found to add two molecules of a base, B, containing a nitrogen or phosphorus donor atom, along the axis normal to the plane of the metal chelate rings and to form a diadduct which is a six-coordinated octahedral complex of nickel(II) (*52–54*) (Fig. 1). Adduct formation of this type is ideally suited for obtaining thermodynamic data on the donor properties of bases with respect to a single reference acceptor molecule, provided the systems are studied in noncoordinating solvents in which the complications involving the displacement of solvated molecules can be avoided.

The magnetic and spectral properties of the planar metal chelate acceptors undergo marked changes when axial coordination occurs, and adduct formation has therefore attracted much attention recently. Analytical chemists have exploited adduct formation for

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* This article will be published later in a volume entitled *Separation Techniques: Proceedings of the Nineteenth Annual Summer Symposium on Analytical Chemistry.*

the purpose of increasing the extent of extraction of metal chelates into organic solvents. With the exception of instances in which the coordinated donors are water molecules, it has been observed that adduct formation in general increases the hydrophobic character of the metal chelates and hence their extractability into organic solvents. The role played by water as a donor molecule in the liquid-liquid extraction of metal chelates has been elucidated in a recent study of the liquid-liquid extraction of bis(8-quinolinolo)-zinc(II), $ZnOx_2$, by a variety of organic solvents. The chelate, $ZnOx_2(H_2O)_2$ was found to extract poorly, but when the two water molecules were successively replaced by organic solvent molecules, the extent of extraction of the zinc chelate increased (55).

In most of the early work an empirical approach was adopted and consisted of the introduction of a neutral donor molecule into the extraction system to obtain an enhancement in the distribution coefficient of the metal chelate. For example, it has been known for some time that the extent of extraction of the copper(II) chelate

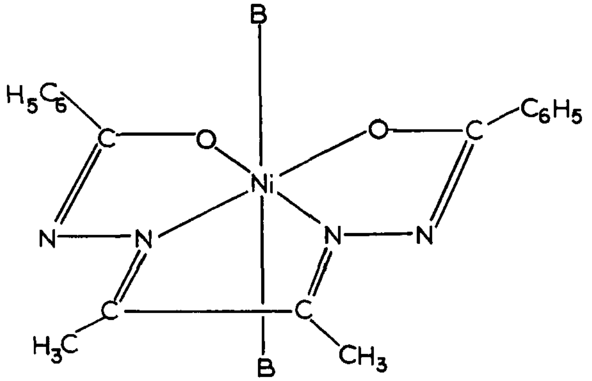


FIG. 1. Diadduct of diacetylbisbenzoylhydrazino nickel(II).

of salicylic acid into an organic solvent is increased by the addition of pyridine to the extraction system (27). The copper(II) chelate of salicylaldehyde is square planar (5); presumably the copper(II) chelate of salicylic acid is also square planar, and the formation of a pyridine adduct which is a five- or six-coordinated copper(II) complex is probably responsible for the enhancement in the distribution coefficient of the metal chelate. It is not always necessary to introduce another donor molecule into the system containing the metal ion and the chelating agent for adduct formation to occur and for the extractability of the metal chelate to increase, since the neutral molecules of excess chelating agent can participate in adduct formation. The chelating agents 8-quinolinol and β-isopropyltropolone have been observed to behave in this manner (*17,56*). It is important to recognize that the addition of an excess of a neutral molecule, which is extremely soluble in the organic phase, will alter the properties of the organic phase. Thus, specific solvation effects, or adduct formation, or both, can contribute to the increased extraction of the metal chelate.

The most widely investigated extraction systems have involved β-diketones as chelating agents and tri-*n*-butylphosphate or tri-*n*-butylphosphine oxide as the neutral donors for the separation of lanthanides and actinides that have oxidation states of III, IV, V, and VI. The extraction behavior of these systems has been described recently in an extensive review (*45*). Owing to the complicated solution chemistry of the lanthanides and actinides, recent work has been directed toward understanding the behavior of simpler analogous systems involving the chelates of divalent transition metal ions, since a great deal of experimental data on their behavior in solution and on the structure and stereochemistry of their complexes are available. In these investigations, the β-diketones have been employed almost exclusively as the chelating agents, the adduct-forming donors being either those that contain nitrogen atoms, such as pyridine, quinoline, or isoquinoline, or those that contain oxygen donors, such as tributylphosphate. In the course of these studies there have been many instances in which adduct formation of metal chelates has been inferred from equilibrium extraction data. In a much smaller number of cases the adducts of certain divalent transition metal chelates have been isolated, characterized, and measurements made on one or more of their physical properties. The purpose of this review is to discuss the structural and stereochemical implications of these results and to evaluate the various factors that influence the formation of metal chelate adducts.

One of the β-diketones whose metal-complexing properties have been thoroughly investigated is acetylacetone. In the last few years the structures of several acetylacetone chelates of the metals of the first transition series have been determined by X-ray techniques. Bis(acetylacetonato) copper(II) was found to be planar (*44,57*); the diaquobis(acetylacetonato) cobalt(II) was shown to have a tetragonally distorted configuration with the two water molecules occupying the two apical sites and the two chelate rings approximately planar (9). The diaquobis(acetylacetonato) nickel(II) chelate has the same structure as the cobalt(II) chelate, (37), but the anhydrous form was found to be trimeric in the solid state (*10*), as well as in benzene solutions (29), each nickel atom being surrounded by a distorted octahedron of oxygen atoms, Fig. 2. It can therefore be anticipated that the copper(II), cobalt(II), and nickel(II) acetylacetonates will form adducts with donors that can displace water molecules in the axial positions perpendicular to the plane of the chelate rings. Some difficulty in adduct formation will, of course, be expected if the trimeric form of nickel(II) acetylacetonate is found to persist in the solvent medium used. Nickel is hexacoordinated in the trimer and is therefore coordinatively saturated. Adduct formation will occur when one or more chelate rings are ruptured or if the donor molecule is attached to an atom other than the nickel ion. In this connection it should be mentioned that in the nickel complex, bis(dimethylglyoximato) nickel(II), the strong axial nickel-nickel bonds (26) prevented the isolation of adducts with strongly basic donors such as pyridine (3). Moreover, the distribution coefficient of the nickel chelate between chloroform and water was not increased in the presence of donors such as quinoline or dodecylamine, whereas these donors were found to enhance the extraction of bis(dimethylglyoximato)copper(II), in which the axial bonds are the relatively weak copper-oxygen bonds (*18*).

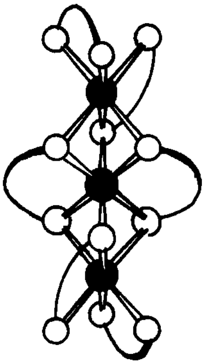


FIG. 2. Trimer of Ni(acac)$_2$. The shaded circles represent nickel atoms and the open circles represent oxygen atoms.

The expectation that the divalent metal acetylacetonates will form adducts has been amply verified. The copper(II) chelates of acetylacetone, benzoylacetone, and ethylacetoacetate form 1:1 adducts with heterocyclic bases such as pyridine or substituted pyridines (*30*) and quinoline (*24*). On exposure to air, the solid adducts slowly undergo decomposition, the heterocyclic base being lost as vapor. From an examination of the infrared and visible spectra of these adducts dispersed in Nujol mulls, it was concluded that the 1:1 adducts were 5-coordinated complexes of copper(II). The additional molecule of the heterocyclic base in the 1:2 adducts obtained with bis(ethylacetoacetato)copper(II) was assumed to be free in the crystal lattice and not coordinated to give a six-coordinated copper(II) complex. The existence of five-coordinated complexes of copper(II) has been convincingly established by a number of X-ray studies (*2*), although it has been recently suggested that at least in some of these cases, five-coordination occurs as a result of a steric hindrance, the approach of a sixth ligand being sterically prevented by one or more atoms in a ligand molecule (*8*).

In contrast to the five-coordinated adducts of copper(II) acetylacetonates, a six-coordinated copper(II) complex was obtained with trifluoroacetylacetone and pyridine. The electronic and infrared spectra of this 1:2 adduct were compared with the spectra of the 1:1 adduct, which was also isolated, and with the spectra of the parent copper(II) chelate. In the infrared region, single peaks were observed for the vibrations of the pyridine molecules; therefore, both pyridine molecules in the 1:2 adducts must have identical environments. It was thus established that in the 1:2 adducts, both pyridine molecules were coordinated to the central copper atom, and that one pyridine molecule was not merely trapped in the crystal lattice (*25*). These spectral studies have also disproved an earlier contention that in the 1:1 adducts one of the chelate rings is opened and the vacant coordination site is occupied by the donor molecule (*59*). That the chelate rings remain intact in the monoadducts of the bis(acetylacetonato) copper(II) chelates, was further confirmed by an examination of the infrared spectra of the quinoline and isoquinoline monoadducts. The absence of a free carbonyl absorption band around 1600 to 1700 cm^{-1} in the spectra of these chelates seems to be convincing evidence that the acetylacetonate chelate rings are not ruptured in adduct formation (*38*).

In an extension of the above studies on adduct formation, the 1:1 and 1:2 adducts of the copper(II) chelates of hexafluoroacetylacetone, thenoyltrifluoroacetone, and trifluoroacetylacetone with 4-methyl pyridine were prepared. The acetylacetone chelate of copper(II) did not form a 1:2 adduct with 4-methylpyridine and formed a relatively unstable 1:1 adduct from which the 4-methylpyridine was gradually lost on standing. The electronic spectra of all these adducts again indicate that they are definite compounds (*62*). When the methyl groups in acetylacetone are successively replaced by the electron-withdrawing CF_3 groups, the stability of the metal chelate, given by the logarithim of the first stepwise formation constant, decreases from 9.2 for copper(II) acetylacetonate, to 6.6 for the trifluoroacetonate, to 2.7 for the hexafluoroacetylacetonate (*12,60*). This decrease in the chelate stability is accompanied by a concomitant increase in the stability as well as the extractability of the adducts. A decrease in electron density around the central metal ion, i.e., an increase in the residual positive charge, is caused by the electron-withdrawing substituents in the acetylacetone ligand. As a result, the metal has an increased tendency to participate in further coordination. Hence, the most stable chelate, copper(II) acetylacetonate, forms the least stable

TABLE 1

Formation Constants of 1:1 Adducts of Nitrogen Donors and Bis(acetylacetonato)copper(II)

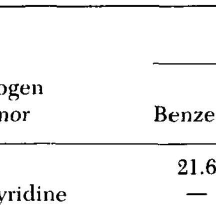
Nitrogen donor	Formation constant in Benzene	Dichloroethane	Chloroform	Acetone	Ref.
Pyridine	7.2; 8.7	—	2.0	4.4	(30)
2-Methylpyridine	—	—	0.66	—	(30)
3-Methylpyridine	6.0	—	—	—	(46)
4-Methylpyridine	10; 10.9	—	2.7	—	(10,30,46,62)
2,6-Dimethylpyridine	—	—	0.23	—	(30)
4-Chloropyridine	5.7	—	—	—	(46)
3-Cyanopyridine	6.8	—	—	—	(46)
3-Acetylpyridine	10.3	—	—	—	(46)
4-Benzoylpyridine	18	—	—	—	(46)
3-Bromopyridine	5.0	—	—	—	(46)
Quinoline	3.7	1.5	—	—	(38)
Isoquinoline	8.6	—	—	—	(38)

adducts, and in fact only a 1:1 adduct has been isolated. The least stable chelate, copper(II) hexafluoroacetylacetonate, forms the most stable adducts, and 1:1 as well as 1:2 adducts, both of which are quite stable, have been isolated (*62*). Thus the statements which were in apparent conflict in the earlier reports concerning the formation of 1:1 and 1:2 adducts of copper(II) acetylacetonates have been resolved.

The formation constants of a number of adducts of copper(II) acetylacetonates have been determined in nonaqueous solvents; the values that have been reported are summarized in Table 1. An extensive calorimetric study of the heats of reaction of a series of pyridine bases with bis(acetylacetonato)copper(II) has also been carried out (*46*). The heats of adduct formation were determined in benzene in the absence of strongly coordinating molecules such as water. Therefore, the heat of reaction should reflect the bond strength of the adduct. A plot of the heat of reaction against the

TABLE 2

Formation Constants of 1:1 Adducts of Nitrogen Donors with Chelates of Copper(II) and Substituted Acetylacetonates (*30*)



Substituent R	Substituent R'	Nitrogen donor	Formation constant in Benzene	Formation constant in Chloroform	Formation constant in Acetone
C_6H_5	CH_3	Pyridine	21.6	2.8	7.5
C_6H_5	CH_3	2-Methylpyridine	—	0.74	—
C_6H_5	CH_3	4-Methylpyridine	—	3.9	—
C_6H_5	CH_3	2,6-Dimethylpyridine	—	0.25	—
OC_2H_5	CH_3	Pyridine	29.0	3.3	15.6
OC_2H_5	CH_3	2-Methylpyridine	9.6	1.6	2.9
OC_2H_5	CH_3	4-Methylpyridine	58.7	8.0	16.0
OC_2H_5	CH_3	2,6-Dimethylpyridine	1.2	0.44	1.6

Hammett sigma constant of the pyridine substituent showed a definite trend. The heats of reaction were high for the stronger bases and decreased to a limiting value as the basicity decreased. However, from the data presented in Table 1 there seems to be no direct correlation between the basicity of the donor molecule and the formation constant of the adduct, probably because the adducts formed are very weak and other effects such as solvation and steric factors overwhelm the weak electronic effects caused by varying the substituents in the donor molecule (*46*).

In contrast to the above results, it was found that the free energies, enthalpies, and entropies of adduct formation of diacetylbisbenzoylhydrazino nickel(II), Fig. 1, with a series of heterocyclic bases, alkylamines, and alkylphosphines, show definite trends (*52–54*). For example, with the alkylamines the donor ability of the amine, as well as the nickel-nitrogen bond strength, increases in a regular manner with the length of the alkyl chains. The reason that these trends are observable in these systems is that the adduct formation constants are several powers of 10 greater than the values obtained with copper(II) acetylacetonates.

Table 2 summarizes the formation constants of the adducts with the copper(II) chelates of a number of substituted acetylacetones. The stabilities of the 4-methylpyridine adducts are greater than the

TABLE 3

Stepwise Formation Constants of Adducts of Oxygen Donors with Metal Chelates of Thenoyltrifluoroacetone

		Solvent				
		Cyclohexane		Carbon tetrachloride	Chloroform	
Metal ion	Oxygen donor	K_{f_1}	K_{f_2}	K_{f_1}	K_{f_1}	Ref.
Zn(II)	Tri-*n*-octylphosphine oxide	—	—	10	—	(*61*)
Co(II)	Tributylphosphate	4.59	2.67	—	—	(*40*)
Cu(II)	Tributylphosphate	3.32	—	2.27	0.65	(*40,56*)
Zn(II)	Tributylphosphate	4.77	—	4.34	2.69	(*40,56*)
Cu(II)	Tri-*n*-butylphosphine oxide	3.98	—	—	—	(*40*)

stabilities of the pyridine adducts as a result of the greater base strength of 4-methylpyridine. The lower stabilities of 2-methylpyridine and 2,6-dimethylpyridine adducts are undoubtedly due to steric effects. Although adduct formation constants have been determined in several solvents, it is not possible to draw any valid conclusions about solvent effects from the data in Tables 1 and 2.

All the adduct formation constants in Tables 1 and 2 have been obtained either from liquid-liquid extraction equilibria studies or have been measured by a spectrophotometric method. The latter method gives reliable values for systems which have rather small formation constants. Recently the formation constant of the 1:1 adduct of the zinc chelate of thenoyltrifluoroacetone with tri-*n*-octylphosphine oxide in anhydrous carbon tetrachloride has been determined by yet another method, which makes use of the nuclear magnetic resonance spectrum of phosphorus (Table 3). This formation constant, as well as the formation constants obtained by spectrophotometric methods in anhydrous media may not be strictly comparable with values that have been calculated from liquid-liquid extraction equilibria data. In extraction studies the organic phase can no longer be considered as an anhydrous medium, because it is invariably saturated with water. The spectrophotometric method is well suited for the determination of adduct formation constants if only a single adduct species is present in solution. If stepwise adduct formation occurs, various adduct species will be found in solution and unless they are unequivocally identified, the formation constants obtained spectrophotometrically are open to question. For example, it has been shown recently that bis(acetylacetonato) cobalt(II), $Co(acac)_2$, forms 1:1 and 1:2 adducts with pyridine as well as a 1:1 adduct of the dimer $[Co(acac)_2]_2$-[pyridine] (*20*). The spectrophotometric method for the determination of adduct formation constants should therefore be used with caution.

It is of interest to investigate the effect of varying the chelated metal ion on adduct formation constants. From the limited data available (Table 3), it can be inferred that the tendency for the zinc(II) chelate to form adducts is greater than that of the cobalt(II) and copper(II) chelates. The usual stability sequence of the transition metal chelates is cobalt(II) < copper(II) > zinc(II); it appears, therefore, that the greater the stability of the metal chelate, the weaker the adduct that is formed. This conclusion was arrived at previously by an examination of the adduct formation constants and corresponding chelate formation constants of copper(II) and a series of substituted acetylacetones.

The study of the thermodynamics of adduct formation of the nickel(II) chelate of diacetylbisbenzoylhydrazone with a variety of donor molecules (*52–54*) has been extended to an investigation of the liquid-liquid extraction behavior of this chelate (*39*). It was shown that the addition of the heterocyclic bases isoquinoline or 4-methylpyridine caused an enhancement of the distribution coefficient of the metal chelate due to the formation of 1:2 adducts. Thus it is clear that the formation of hydrophobic adducts is primarily responsible for the increase in extractability of the nickel chelates into organic solvents. The formation constants of the adducts of the nickel(II) chelates of diacetylbisbenzoylhydrazone are several powers of 10 greater than the formation constants of the adducts of acetylacetone chelates (Tables 1, 2, and 3). The nickel-donor atom bonds in the adducts of the diacetylbisbenzoylhydrazino nickel(II) chelates are therefore much stronger than the corresponding bonds in the adducts of the acetylacetone chelates. Nevertheless, there can be no doubt that the extraction of the chelates of copper(II), cobalt(II), zinc(II), and nickel(II) with acetylacetone and substituted acetylacetones is enhanced by adduct formation with nitrogen- or oxygen-containing donor molecules.

For any meaningful correlations to be made between the structure and properties of metal chelate adducts, their extraction behavior, formation constants, spectra, and magnetic properties must be studied in addition to their structures. To this end, an investigation of the adducts of the chelate, bis-(O,O′-diethyldithiophosphato)nickel(II), $Ni(dtp)_2$, with a series of donor molecules has been initiated in this laboratory. The chelate, $Ni(dtp)_2$, is diamagnetic and its structure has been predicted to be essentially square planar (*41–43*), from the results of an examination of its ligand field transitions. The planarity of the chelate rings has been confirmed in this laboratory by means of a single-crystal three-dimensional X-ray structure determination (*21*). $Ni(dtp)_2$ forms purple monoclinic crystals ($a = 10.48$ A, $b = 10.22$ A, $c = 8.62$ A, and $\beta = 102.5°$) in the space group $P2_1/c$ with two molecules in the unit cell. The structure was solved in projection down the c axis with the special position of the nickel atom chosen as the origin. The four atoms in the chelate ring were found to lie in a plane and the carbon atoms in the ethyl groups were found to adopt a staggered configuration. The important bond distances and bond angles in the chelate ring are shown in Fig. 3. The average nickel-sulfur bond distance is 2.21 A and the average sulfur-phosphorus bond distance is 1.97 A. The values of the bond angles show that there is a significant distortion from square planarity, caused by strain in the four-membered ring. The nickel-sulfur bond distance compares well with the normal value in tetracoordinated diamagnetic nickel chelates (7), and the sulfur-phosphorus bond distance is identical with that found in the potassium salt of O,O′-dimethylphosphorodithioic acid (*15*).

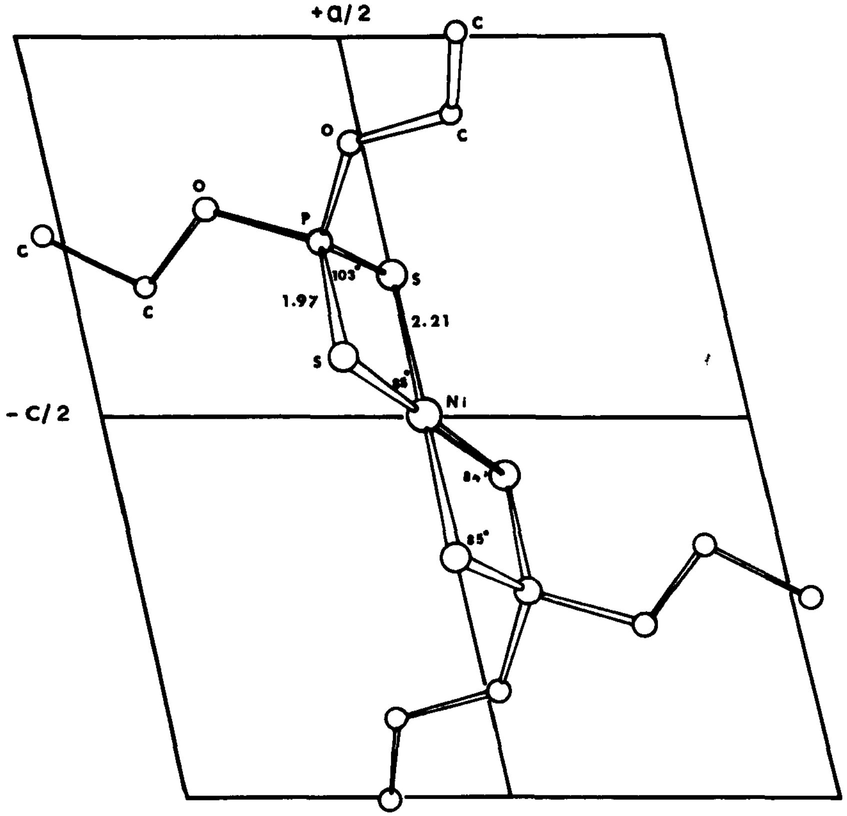


FIG. 3. [010] projection of the structure of $Ni(dtp)_2$. Only one of the two molecules in the unit cell is shown.

Single crystals of the paramagnetic 1:2 pyridine adduct, Ni(dtp)$_2$·2py, have been prepared. Although a five-coordinated 1:1 pyridine adduct of Ni(dtp)$_2$ could not be isolated, evidence for its existence in benzene solution has been found in the course of a spectrophotometric determination of the formation constants of the 1:2 adduct. The values of the successive stepwise adduct formation constants in benzene were found to be 29 and 78 (*13*). Crystals of the 1:2 adduct are unstable in air: their green color changes slowly to the purple color of Ni(dtp)$_2$. However crystals of the adduct when sealed in a thin-walled capillary were found to be stable to X rays. A single-crystal three-dimensional X-ray structure deter-

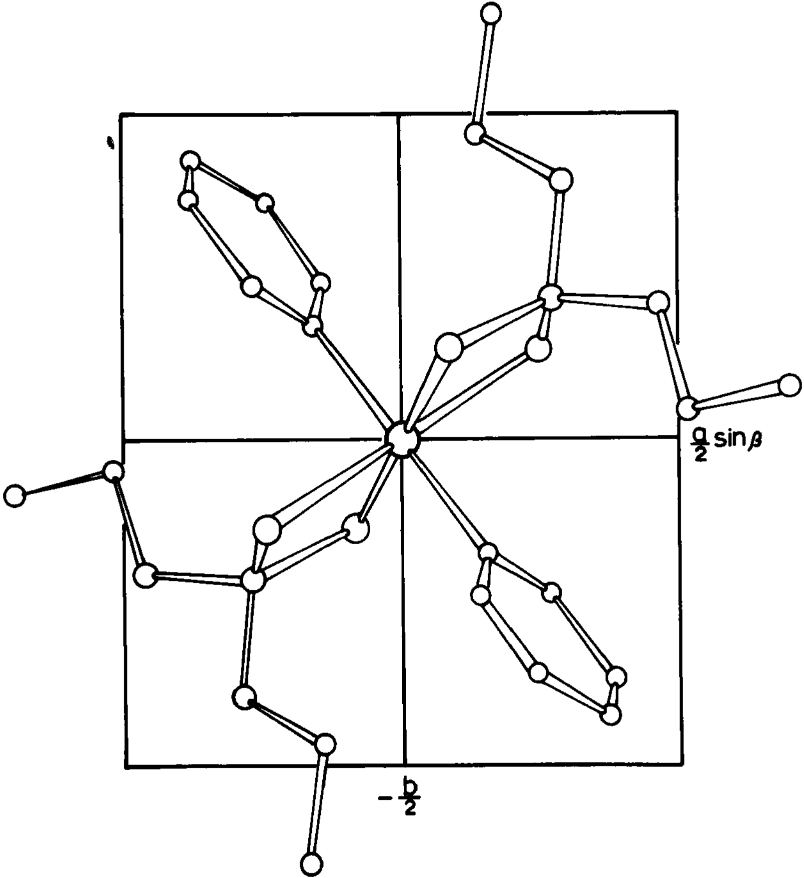


FIG. 4. [001] projection of the structure of the diadduct of Ni(dtp)$_2$ with pyridine. Only one of the two molecules in the unit cell is shown.

mination of this compound is in progress in this laboratory (*51*). The adduct, Ni(dtp)$_2$·2py forms green monoclinic crystals ($a = 8.11$ A, $b = 17.89$ A, $c = 9.94$ A, $\beta = 104.8°$) in the space group $P2_1/c$ with two molecules in the unit cell. This diadduct must therefore have a *trans* configuration. The structure was solved in projection down the a and c axes and was found to have the same features as the parent chelate Ni(dtp)$_2$. One significant difference is that the nickel-sulfur bond distance is increased to 2.46 A. This is to be expected for hexacoordinated paramagnetic nickel chelates (*7*). The plane of the pyridine ring is perpendicular to that of the chelate rings and approximately bisects the larger sulfur-nickel-sulfur angle; the nickel-nitrogen bond distance is approximately 2.1 A. These preliminary results represent the first structure determination of a metal chelate adduct (Fig. 4).

The structures of the metal acetylacetonate adducts are of considerable importance, but little attention seems to have been paid to this area. In cases where the metal ion is coordinatively saturated, the position of attachment of the donor molecule cannot be surmised and has to be determined by a direct experimental method. Although it is possible that the donor molecule will occupy a coordination position which is left vacant by the opening of a chelate ring, there has been no convincing experimental proof that such an adduct exists. Recently, however, liquid-liquid extraction data have been obtained which strongly suggest that ring opening followed by adduct formation occurs. The effect of tri-*n*-octylphosphine oxide on the distribution coefficients between cyclohexane and water of the coordinatively saturated chelates of cobalt(III) and iron(III) with acetylacetone has been determined. It was found that the distribution coefficient of only the labile-iron(III) acetylacetonate showed a marked enhancement, whereas the distribution coefficient of the inert cobalt(III) complex was virtually unchanged. It has been suggested that the only satisfactory explanation of this data consists of the assumption that a chelate ring is ruptured and the molecule of tri-*n*-octylphosphine oxide is coordinated directly to the iron atom (*1*). Confirmation of this interesting hypothesis must await further work with this and related systems.

If the metal ion is coordinatively unsaturated, the donor molecule will occupy a position in the coordination sphere of the metal ion. In such cases, the metal-donor atom bond strength can vary considerably, and any experimental data that can elucidate this aspect of the structure of the adduct are of importance. One approach that can be adopted is to carry out the measurement of free energies, enthalpies, and entropies of adduct formation as well as the examination of spectral data of the adducts. However, little experimental data of this type is available from which the structures of the adducts with metal acetylacetonates can be deduced. Moreover, no complete X-ray structural data on any of these adducts are available, although adducts of cobalt(II) and nickel(II) acetylacetonate with pyridine, aniline, and ammonia have been known for more than 50 years (*6*).

An examination of the infrared spectrum of the bispyridine adduct of nickel(II) acetylacetonate has shown that all the bands in the region below 700 cm^{-1}, which involve Ni—O stretching vibrations, are shifted to lower frequencies. The band at 452 cm^{-1} which arises from an almost pure Ni—O stretching mode is shifted to 439 cm^{-1} in the adduct, owing to a marked change in the Ni—O stretching force constant. This can only be attributed to direct bonding between the metal ion and the nitrogen atom of the pyridine donor. On the basis of this evidence, a *trans* octahedral configuration was proposed for the bispyridine adduct of bis(acetylacetonato) nickel(II) (*49*). This has been recently confirmed by a determination of the space group in which the compound crystallizes. Since the compound crystallizes in the space group $P2_1/c$ with two molecules per unit cell, the compound must have a center of symmetry, and the only possible arrangement of the two pyridine molecules is therefore in a *trans* configuration (*32*). The bispyridine adduct resembles the dihydrate of bis(acetylacetonato)nickel(II), which has been shown, by a three-dimensional X-ray study, to have a *trans* configuration (*48*).

The oxygen atoms in the chelating agent, acetylacetone, can frequently participate in the formation of bridged complexes. For example, bis(acetylacetonato) nickel(II) exists as a trimer in the solid state (*11*) as well as in hydrocarbon solvents (*19*). A three-dimensional X-ray structure determination of the trimer has shown that each nickel ion is surrounded by a distorted octahedron of oxygen atoms (*11*). A monoadduct with pyridine and a dimeric form of the nickel chelate has been isolated with the stoichiometry $[Ni(acac)_2]_2 \cdot py$ in addition to a 1:2 adduct, $Ni(acac)_2 \cdot 2py$ (*19*). The structure of the monoadduct has not been determined. If how-

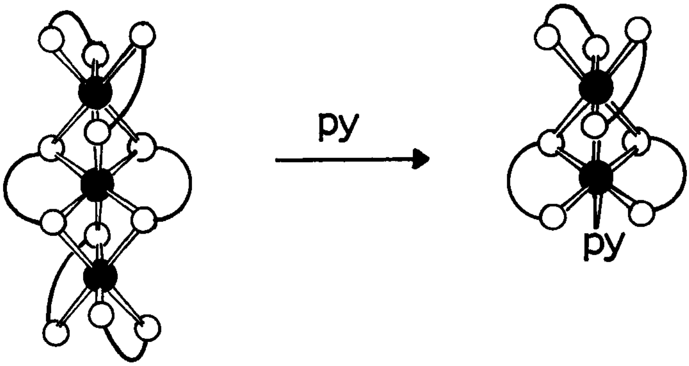


FIG. 5. Probable structure of the monoadduct of $[Ni(acac)_2]_2$ with pyridine. The shaded circles represent nickel atoms and the open circles represent oxygen atoms.

ever, it is assumed that the octahedral configuration of the nickel ion is maintained by the sharing of octahedral faces, the adduct, $[Ni(acac)_2]_2 \cdot py$ probably has the structure in Fig. 5, since it is the only adduct to be expected when the dimer breaks away from the trimer. An X-ray structure determination of this compound would be of great interest.

Although no stable monoadduct of pyridine with bis(acetylacetonato) nickel(II) has been found (*19*), a stable monoadduct with bis(acetylacetonato) cobalt(II) has been isolated, together with the pyridine diadduct and the monoadduct of the dimeric species, $[Co(acac)_2]_2 \cdot py$ (*20*). It may be speculated that the structures of

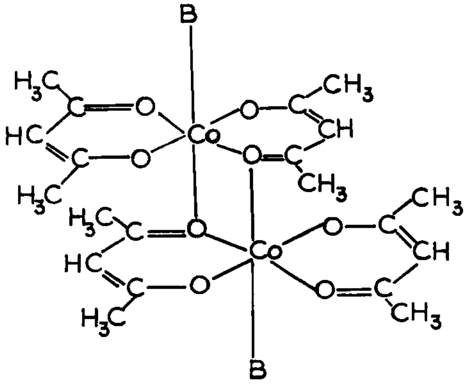


FIG. 6. Probable structure of the diadduct of $[Co(acac)_2]_2$ with a nitrogen donor.

the latter two compounds are similar to the structures of the corresponding nickel(II) compounds, but they may well be different. It has, for example, been proposed that the mono adduct with cyclohexylamine is the dimer, $[Co(acac)_2]_2 \cdot 2B$, having the structure shown in Fig. 6 (*4*), and it would not be entirely unexpected if the monopyridine adduct had a similar structure. On the other hand, the monoadduct of pyridine with $Co(acac)_2$ may be a five-coordinated cobalt(II) chelate with a square-pyramidal configuration, or a trigonal bipyramidal configuration, or a structure intermediate between the two, as was found for $Zn(acac)_2 \cdot H_2O$ (*47*). The observation that the only monoadducts isolated were $[Ni(acac)_2]_2 \cdot py$ with pyridine as the donor (*19*), and $Ni(acac)_2 \cdot py$ with methylpyridines as donors (*29–30*), suggests that the nature of the nitrogen-containing base is probably a factor that determines the type of adduct formed (*4*). Verification of this interesting conclusion must await the X-ray structure determination of these adducts.

The manganese(II) chelate of acetylacetone forms the adduct $Mn(acac)_2 \cdot py$, and the monopyridine adduct of the dimeric form, $[Mn(acac)_2]_2 \cdot py$. These compounds resemble the corresponding adducts of the acetylacetonates of nickel(II) and cobalt(II). The five-coordinated manganese(II) adducts, in which two molecules of the heterocyclic base are coordinated to the chelate, are very unstable and in this respect they differ markedly from the nickel(II) and cobalt(II) adducts, but resemble the behavior of the zinc(II) adducts (*28*).

Five-coordinated zinc(II) complexes are known (*31,47*), and it is probable that the adducts of the type $ZnX_2 \cdot B$ (where B ≡ tri-*n*-butylphosphate and X ≡ thenoyltrifluoroacetone) are five-coordinated zinc(II) complexes with a pyramidal arrangement of the bonding atoms (*47*). Adducts of bis(acetylacetonato) zinc(II) with two molecules of ammonia, one molecule of o-phenanthroline, or one molecule of bipyridyl have also been reported (*16*). The diadduct with ammonia probably has an octahedral configuration, but the structures of the monoadducts with bipyridyl and with *o*-phenanthroline depend on whether the donors are monodentate or bidentate in these adducts.

It is well known that the square-planar copper(II) complexes expand their coordination number from four to five, with the result that square-pyramidal complexes are formed (*2,63*). On these grounds it appears reasonable to postulate similar structures for the monoadducts formed with bis(acetylacetonato) copper(II) chelates and a wide variety of donor molecules.

The adducts of the metal acetylacetonates have been by far the most extensively investigated complexes. Several questions of importance that concern the properties of adducts have been clarified. The available thermodynamic data have shown that in the absence of specific steric and solvation effects, the greater the basicity of the donor atom, the greater the stability of the adduct that is formed, and that the greater the stability of the metal chelate, the weaker the adduct that is formed. The adducts formed with oxygen- and nitrogen-containing donor molecules and the acetylacetonates of certain of the first row transition metals have enhanced hydrophobic properties, and, as a consequence, their distribution coefficients between an organic phase and aqueous phase are increased. Although it is premature to classify these adducts on the basis of their structures, which are mostly unknown, it is clear from the foregoing that the adducts of the metal acetylacetonates, and indeed the adducts of all metal chelates, must fall into one of the following classes:

Class I. Adducts formed by coordination of the chelated metal ion to one or more donor groups. Strong bonds are formed, the configuration of the metal chelate is altered, or its structure is grossly distorted. In extreme cases the adduct formed can be considered to be a charge-transfer complex. Examples of adducts in this class are $Ni(dtp)_2 \cdot 2py$, $Zn(TTA)_2 \cdot TBP$, and $Ni(acac)_2 \cdot 2py$.

Class II. Adducts formed by the weak interaction of the metal ion with donor molecules. The structure of the metal chelate is hardly affected by the weak bonds formed between the metal chelate and the donor, but the coordination number of the metal ion increases. Because of the weak bonds formed, only the monoadduct is sufficiently stable to be isolated, e.g., $Cu(acac)_2 \cdot py$.

Adducts that fall into classes I and II are formed with coordinatively unsaturated metal chelates, whereas those that fall into classes III and IV are formed with coordinatively saturated metal chelates.

Class III. Adducts in which the donor molecule occupies a position in the coordination sphere of the metal ion that is vacant as a result of the rupture of a chelate ring. The coordination number of the metal does not change. An example of such an adduct is

$[Ni(acac)_2]_2 \cdot py$, which is formed by the rupture of the chelate rings in the trimer $[Ni(acac)_2]_3$. The coordination number of nickel is six in both complexes. Another probable example is the adduct of tri-*n*-butylphosphine oxide with $Fe(acac)_3$, in which one of the chelate rings is ruptured and the vacant position is occupied by the TBPO donor (*1*).

Class IV. In adducts of this class, the donor molecule is attached to an atom other than the chelated metal atom and the coordination number of the metal remains unchanged. No example of this class of adduct has been found with the divalent transition metal acetylacetonates. With the acetylacetonate of iron(III), a diadduct with chloroform has been identified which probably falls into class IV. It has been suggested that the two molecules of chloroform are held by hydrogen bonds between layers perpendicular to the *b* axis of the tris(acetylacetonato) iron(III) chelate (*58*). A similar structure has been proposed for the adducts of several halomethanes with the acetylacetonates of the tervalent ions, aluminum, iron, chromium, scandium, gallium, and indium, on the basis of a preliminary study of their NMR spectra (*14*). There are experimental difficulties associated with the location of the site of attachment of a donor molecule such as chloroform, since the bonds formed between the donor atom and the metal-chelate acceptor are quite weak. This is evident in the chloroform and benzene adducts of the zinc(II) chelate of 8-quinolinol (*55*), although it is probable that these adducts too can be grouped together in class IV.

Examples of class IV adducts are more likely to be found with the chelates of metal ions having higher oxidation states. It has been suggested from equilibrium extraction data involving the thorium chelate of thenoyltrifluoroacetone, TTA, in the presence of tri-*n*-octylamine, R_3N, that the adduct formed is $Th(TTA)_4 \cdot R_3NHCl$ and that the amine hydrochloride is bound by one of the TTA molecules and not by the thorium (*50*). The TTA chelates of a number of other elements in the lanthanide and actinide series were found to form adducts with organophosphorus compounds such as tri-*n*-butylphosphate, TBP, and tri-*n*-octylphosphine oxide, TOPO. Many stable adducts have been isolated from the liquid-liquid extraction systems involving these compounds (*22,33–36*). A study of the infrared spectra of these adducts indicates that the TTA molecules are monodentate as well as bidentate in several representative examples and that the organophosphorus donor molecules are directly attached to the metal ion (23). Again, no structural investigations on these compounds have been carried out, and it is possible that examples of class IV adducts may be found among this group of compounds.

Acknowledgment

Financial assistance from the National Science Foundation Institutional Grant to the University of Arizona is gratefully acknowledged.

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Received by editor July 6, 1966
Submitted for publication July 21, 1966