have been characterized by their X-ray diffraction, optical absorption, and morphological features.

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Adsorptive and Catalytic Properties of Isolated Units of $[Fe_4S_4(SR)_4]^{2-}$

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Abstract: Reaction of 3-mercaptopropyltrimethoxysilane with wide pore silica gel produced a gel with surface $\equiv SiCH_2CH_2CH_2SH$ groups. Exchange between RS- groups occurred when this material was exposed to $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu)_4N]_2$ in acetonitrile, to produce a silica gel containing the Fe_4S_4 unit bound to the surface with accompanying $n\text{-}Bu_4N^+$ counterions. Since the $n\text{-}Bu_4N^+$ ion decomposed at about 110 °C, a gel in which this ion had been replaced by Ca^{2+} was also prepared. These Fe_4S_4-attached gels exhibited no catalytic activity for the hydrogenation of carbon monoxide, ethylene, propylene, 1,3-butadiene, or acetylene at 25–250 °C nor for the oxidation of hydrogen, carbon monoxide, ethylene, or 1,3-butadiene at 25–100 °C. Significant adsorption of carbon monoxide and hydrogen appeared only at subzero temperatures and it was not clear whether such adsorption should be characterized as strong physisorption or very weak chemisorption.

Although the primary biochemical function of the complex $[Fe_4S_4(SR)_4]^{2-}$ appears to be electron transfer, the question inevitably arises as to whether these units have separate catalytic activity.[1] Holm has suggested that "it is entirely probable that dihydrogen activation and heterolytic cleavage, evidenced by H/D exchange, occurs at a 4-Fe site", and he noted that hydrogenase is an iron-sulfur enzyme which contains no other metals or prosthetic groups.[1] The only clear case of catalysis by a molecular Fe_4S_4 complex is that reported by Schwartz and van Tamelen[2] in which $[Fe_4S_4(SC_2H_5)_4]^{n-}$ catalyzes the α,α addition of thiols to isocyanides. The reduced unit with $n = 4$ was somewhat more active than the unit with $n = 2$. Averill and Orme-Johnson[3] have reported a study of the interaction of hydrogen and carbon monoxide with $[Fe_4S_4(SPh)_4]^{n-}$ in *N,N*-dimethylacetamide. Exposure to carbon monoxide for $n = 3$ results in the appearance of an EPR signal which decreases upon removal of the carbon monoxide. Exposure to hydrogen does not generate an EPR signal. The authors suggest that hydrogen is heterolytically dissociated in hydrogenase with a hydride ion becoming attached to an iron atom and a proton to some basic group attached to the imbedding protein.

The work of the present paper was undertaken on the view that it would be useful to know how the Fe_4S_4 unit behaved when it was in the most inert environment possible. To this end, we have avoided the presence of solvents and have exposed the Fe_4S_4 unit directly to gas-phase adsorptives and reactants. Silica gels have been prepared which contain $\equiv SiCH_2CH_2CH_2SH$ groups at the surface and Fe_4S_4 units have been attached to this thiol-modified gel by RS exchange with $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu_4N)_2]$. A similar procedure has been used to attach Fe_4S_4 units to the surface of a tin oxide electrode.[4] Our objective was to assess the degree to which the isolated Fe_4S_4 unit behaves as a coordinatively unsaturated species to carbon monoxide and hydrogen and to ascertain whether it possesses any catalytic activity in hydrogenation and oxidation reactions.

Experimental Section

Thiol-Modified Silica Gel. Davison grade 62 silica gel (70–80 mesh, nominal pore diameter 14 nm, specific pore volume 1.1 $cm^3\ g^{-1}$, specific area 285 $m^2\ g^{-1}$) was washed successively with 0.1 M nitric acid and water to a pH of 7. It was then dried in flowing helium at 160 °C. The modification was effected as previously described[5] by refluxing 10 g of gel and 6 g of redistilled 3-mercaptopropyltrimethoxysilane in 100 cm^3 of *m*-xylene for 24 h under flowing nitrogen. The gel was washed successively with *m*-xylene and acetonitrile until silver nitrate in acetonitrile gave a negative test for mercaptan. The gel was dried in vacuo at 100 °C for 1 h. Microanalysis for C, N, and S led to calculated coverages for various preparations which ranged between 1.35 and 1.67 molecules of silane attached per nm^2 (0.578–0.709 mmol g^{-1}). During preparation, some of the thiol groups appeared to have become converted to disulfide groups, since use of Ellman's reagent[6] gave surface concentrations of sulfhydryl groups between 0.77 and 0.84 per nm^2.[7] This number was not affected by exposure of the gel to air.

Preparation of (Fe_4S_4)-Attached Gel. The iron-sulfur complex $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu_4N)_2]$ was prepared by the method of Holm[8] and recrystallized from acetonitrile–methanol. It exhibited the correct melting point and visible spectrum and satisfactory analyses for C, H, N, S, and Fe. This compound was reacted with the thiol-modified silica gel in Schlenck-type glassware by bubbling nitrogen through

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Table I. Adsorption of Carbon Monoxide[a] Irreversible at −78 °C on Fe_4S_4 Gels

counterion	(Bu_4N^+)[b]		(Ca^{2+})[c]	
	T_{act}, °C	adsorption, μmol g^{-1}	T_{act}, °C	adsorption, μmol g^{-1}
	25	5.7	25	32.4
	50	6.8	60	41.2
	100	10.6	100	41.2
	110	21.0		
	160	24.3	150	44.6
	185	24.7	200	50.0
	225	24.1		
	300	23.3		

[a] Exposed to carbon monoxide at −78 °C for 15 min. [b] 1.4% Fe or 63 μmol Fe_4S_4 g^{-1}. [c] 1.6% Fe or 72 μmol g^{-1}.

Table II. Amount of Adsorption of Carbon Monoxide and Hydrogen Irreversible at Various Temperatures on $CaFe_4S_4$ Gels[a]

T, °C	CO/Fe_4S_4[b]	T, °C	H_2/Fe_4S_4[c]
−126	0.93	−196	0.43
−78	0.71	−160	0.21
0	0.09	−127	0.05
25	0.00	−78	0.00

[a] T_{act} = 150 °C, exposed to adsorptive for 15 min before flushing with helium for 60 min. [b] 0.83% Fe or 38 μmol Fe_4S_4 g^{-1}. [c] 1.6% Fe or 72 μmol Fe_4S_4 g^{-1}

2 g of the modified gel suspended in a solution of 0.1-0.5 g of the (Fe_4S_4) compound in 60 cm^3 of acetonitrile for 20 h at 25 °C. The mixture was then heated to 65 °C for 1 h to facilitate elimination of the *tert*-butyl mercaptan formed by exchange with surface SH groups. The resulting almost black gel was washed with five portions of acetonitrile and dried in vacuo at 80 °C. In some cases, the $(n\text{-}Bu)_4N^+$ groups were replaced by Ca^{2+} by slowly percolating 6 g of $Ca(NO_3)_2{\cdot}4H_2O$ in 100 cm^3 of methanol through a bed of the gel, washing it successively with methanol and acetonitrile, and drying it in vacuo at 80 °C. All operations were effected under thoroughly deoxygenated nitrogen including transfer of the Fe_4S_4-attached gel to the reaction system.

Analysis for iron was performed by digestion of the gel with a mixture of nitric and sulfuric acids followed by spectrometric analysis of the complex with 1,10-phenanthroline.[9] Microanalyses for C, N, and S were consistent with the replacement of three to four of the *t*-BuS- groups by σ-S- (where σ denotes the surface or some group attached thereto). Experimental error does not permit one to distinguish between the replacement of three and four *t*-BuS- groups, but one would expect replacement of more than three *t*-BuS- groups to be difficult sterically. The gel was treated in some cases with a solution of the thiophenol in acetonitrile according to the method of Holm.[10] This solution extracted $[Fe_4S_4(C_6H_5S)_4][(n\text{-}Bu)_4N]_2$ (λ_{max} 455 nm) or the Ca^{2+} analogue (λ_{max} 445 nm) from the gels.

Apparatus. The apparatus resembled that employed in this laboratory for studies of adsorption.[11] Ultrapure helium was employed as the carrier gas and its content in oxygen was kept below 0.1 ppm at the bed of Fe_4S_4 gel. Fe_4S_4 gel (0.5-1 g) was activated in flowing helium and then exposed to carbon monoxide or hydrogen at a selected temperature. The gel was then flushed with helium at the same temperature for 60 min. After this, the gel was quickly warmed to room temperature to release the adsorbate as a sharp pulse for catharometric measurement. Hydrogen was converted to water by passage over CuO at 500 °C before entering the catharometer.

Adsorption. Table I shows the amounts of carbon monoxide adsorbed irreversibly at −78 °C (i.e., retained on the adsorbent at −78 °C but released on warming to 25 °C) as a function of the temperature of activation, T_{act}, in flowing helium for 90 min. When $(Bu_4N)_2Fe_4S_4$ gel was heated at 110 °C or higher, the cation decomposed to form a material to be designated $H_2Fe_4S_4$ gel. The products of decomposition were trapped and analyzed by gas chromatography. They consisted of tributylamine, butylenes, and traces of other compounds. Nothing was detected during activation of $CaFe_4S_4$ gel even at 200 °C and extraction of the gel with thiophenol after activation led to recovery of $[Fe_4S_4(C_6H_5S)_4]Ca$. Adsorption of carbon monoxide on the activated gels was not immediate. Thus, the irreversible adsorption of carbon monoxide was measured at −78 °C on a sample of $CaFe_4S_4$ which had been activated at 150 °C. After an exposure to carbon monoxide of 15 min, the adsorption was 0.578 cm^3 (0.571); after 30 min, 0.624 cm^3; and after 60 min, 0.709 cm^3 (0.701). The values in parentheses are those obtained from a repetition of the experiment. The rate of adsorption of hydrogen was also slow. Adsorption from a pulse of hydrogen passed over the $CaFe_4S_4$ gel at −196 °C was negligible but adsorption was apparently complete after exposure to hydrogen for 10 min.

Table II exhibits the results of measurement of the amounts of carbon monoxide and hydrogen held irreversibly at various temperatures on samples of $CaFe_4S_4$ silica gel which had been activated at 150 °C. The following amounts of carbon monoxide were held irreversibly on the thiol-modified gel itself (with no Fe_4S_4 complex) after activation at 160 °C and exposure to carbon monoxide for 15 min: −126 °C, 0.010 mmol g^{-1}; −78 °C, 0.0044 mmol g^{-1}. Negligible carbon monoxide was adsorbed when one pulse was passed over the thiol-modified gel at these temperatures, but the adsorbent appeared to be saturated by an exposure to carbon monoxide for 5 min. No hydrogen was retained by the thiol-modified gel at −196 °C. The data in Tables I and II have been corrected for the adsorption of carbon monoxide on the thiol-modified gel alone.

Exposure to oxygen of a solution in acetonitrile of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu)_4N]_2$ resulted in rapid oxidation and destruction of the Fe_4S_4 core. However, a 0.5-cm^3 pulse of oxygen in helium carrier flowing at 30 cm^3 passed without loss through samples of $CaFe_4S_4$ and $(Bu_4N)_2Fe_4S_4$ gels at 25 and at 100 °C. At higher temperatures, reaction began and carbon dioxide was evolved. A sample of the $CaFe_4S_4$ gel reacted when exposed continuously to dry oxygen at 25 °C, but reaction was slow. The starting gel turned a dark red and then a golden yellow over an interval of about 15 min. If the gel was wet with acetonitrile or water, reaction occurred quickly.

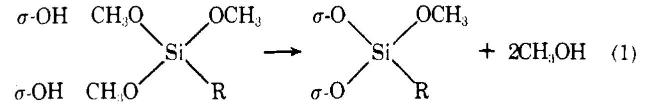
Catalytic Activity. Activity for the catalytic hydrogenation of carbon monoxide, ethylene, propylene, 1,3-butadiene, and acetylene was tested in a pulse reactor. Pulses of about 1 cm^3 of these gases were injected into hydrogen which flowed over about 0.5 g of Fe_4S_4-attached silica gel at 3-120 cm^3 min^{-1}. Hydrogen was passed through the bed of gel for 1.5 h at 25 °C before the first injection. Hydrogen was then passed for 1.5 h at a higher temperature and pulses of hydrocarbon were injected at that temperature. The operation was repeated at a still higher temperature. Possible hydrogenation was also investigated by trapping a pulse in the catalyst tube at various temperatures for about 1 h and then restoring the flow of hydrogen. No hydrogenation was detected in any experiment with $CaFe_4S_4$ (25-250 °C) or $(Bu_4N)_2Fe_4S_4$ (25-100 °C). In these experiments the gel was first pretreated with hydrogen and run at 25 °C. The operations were repeated at progressively higher temperatures to the limit shown after which hydrogenation was tested at 25 °C. The $(Bu_4N)_2Fe_4S_4$ gel was decomposed at 150 °C to generate $H_2Fe_4S_4$. No hydrogenation activity could be detected in the range 25-250 °C on this material.

Pulses of oxygen mixed with the compounds hydrogen, carbon monoxide, ethylene, and 1,3-butadiene were passed over the gels just mentioned in helium carrier at 25-100 °C. No products of oxidation were detected. $CaFe_4S_4$, $(Bu_4N)_2Fe_4S_4$, and $H_2Fe_4S_4$ were pretreated in hydrogen at 150, 100, and 150 °C, respectively.

To test for the possible formation of singlet oxygen[12] during reaction between oxygen and the three gels mentioned above, 1,3-cyclohexadiene in methylene chloride, 0.5 gel, and oxygen at a pressure of 1 atm were stored for 24 h at 25 °C. The Fe_4S_4 core reacted with the oxygen but no formation of 1,4-peroxycyclohexane was detected.

Discussion

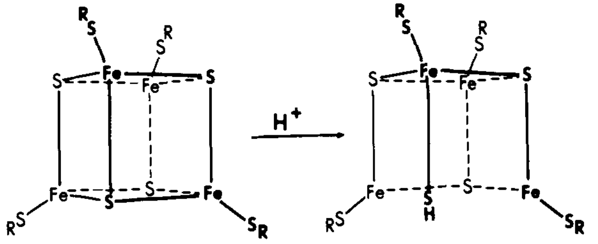
Reaction of $RSi(OCH_3)_3$ with the silanol groups of silica gel occurs on the average according to eq 1.[5] In effect, one



(1)

generates a silica gel extended by one layer of Si and with the group R replacing some of the surface silanol groups. When the thiol-modified gel (R = $CH_2CH_2CH_2SH$) was immersed

Scheme I



in a solution of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu_4N)_2]$, rapid substitution of σ-$CH_2CH_2CH_2S$ for t-BuS occurred. Between three and four molecules of t-BuSH were displaced per Fe_4S_4 unit. The thiol-modified gels contained about 1.5 atoms of sulfur per nm^2, but about 40% of these may have become converted to disulfide linkages. The Fe_4S_4-attached gels contained about 0.13 Fe_4S_4 unit per nm^2 and an equal number of equivalents of n-Bu_4N^+ or Ca^{2+}. In the original silica gel each granule was 71% void by volume and the nominal pore diameter was 14 nm. The modification reduced these numbers, but the gels still had an open structure.

To remove any possibly coordinated solvent, the gel was initially treated in flowing helium in the measurement apparatus to various temperatures. Decomposition of the n-Bu_4N^+ anions began to occur at about 110 °C by the reaction

$$n\text{-}Bu_4N^+ \rightarrow n\text{-}Bu_3N + \text{butylene} + [H^+] \qquad (2)$$

We do not know where the two protons per Fe_4S_4 core go. The designation $H_2Fe_4S_4$ which is used for the product of the decomposition implies no specification of structure. Following Bruice,[13] the reaction with the first proton might involve Scheme I and the addition of the second proton would involve further opening of the Fe_4S_4 unit. However, Johnson and Holm[14] have presented evidence that the proton initially reacts with $Fe_4S_4(SR)_4{}^{2-}$ in N-methylpyrrolidone to form RSH without destruction of the core. The products of decomposition of the Fe_4S_4-attached gels with n-Bu_4N^+ counterions gave only traces of t-BuSH and very small amounts (~1% of n-Bu_3N) of unidentified materials which might have been disulfides. To avoid the formation of these gels of uncertain structure, gels were prepared in which n-Bu_4N^+ was exchanged by Ca^{2+}. These gels exhibited no sign of decomposition even at 250 °C and, after activation at 200 °C, treatment with thiophenol extracted $[Fe_4S_4(SC_6H_5)_4]^{2-}$.

Adsorption. Any adsorption of hydrogen and carbon monoxide on Fe_4S_4-attached gels at 25 °C was so weak that adsorbed hydrogen and carbon monoxide were rapidly removed by flushing with helium at 25 °C. If ΔH of adsorption is negative, then, if the temperature is lowered far enough, the rate of desorption into flowing helium will become so slow that one may say that the adsorption has become irreversible. Even physisorption will become irreversible at low enough temperatures.

At −78 °C, both the $(n\text{-}Bu)_4N^+$ and the Ca^{2+} gels retained carbon monoxide as shown in Table I. The amount retained by the $(n\text{-}Bu)_4N^+$ gel increased with increasing T_{act} and particularly noticeably in the temperature range at which decomposition had been noted, ~110 °C. The ratio CO_{ads}/Fe_4S_4 was nearly unity on the Ca^{2+} gel at −126 °C, still substantial at −78 °C, but small at 0 °C. Significant amounts of carbon monoxide are physisorbed irreversibly on the thiol-modified gel itself at −126 and −78 °C. The entries in Tables I and II have been corrected for this adsorption.

Should the adsorptions of Tables I and II be classified as strong physisorption or very weak chemisorption? The very large optical absorption of these gels prevented a test of this question by optical spectroscopy. However, comparison of the adsorption of carbon monoxide on the $(Bu_4N)_2Fe_4S_4$ and the $CaFe_4S_4$ gels suggests that the sites for adsorption of carbon monoxide on the $CaFe_4S_4$ gels are the Ca^{2+} ions. Egerton and Stone[15] found that one molecule of carbon monoxide was adsorbed at each exposed Ca^{2+} ion in CaY zeolite with a heat of adsorption of 40–45 kJ mol^{-1}. It can be difficult to decide whether adsorptions of the strengths of those found here are best represented as involving a polarization bond or a more definite coordination of the adsorbate to the site for adsorption.[16] In any case, these adsorptions are no stronger than some strong physisorptions.[17]

The rate of reaction of Fe_4S_4-attached gels with oxygen is much slower than that of oxygen with $[Fe_4S_4(SR)_4]^{2-}$ in solution.[2] No loss of oxygen could be detected from a pulse of oxygen passed over $CaFe_4S_4$ gel at 25 and 100 °C, but reaction did occur slowly upon continuous exposure to oxygen at 25 °C. If the gel was wet with water or acetonitrile, reaction was about as rapid as in solution. It appears that the oxidation involves some ionic transition state favored by polar solvents.

Catalytic Activity. The possible activity for the hydrogenation of carbon monoxide, ethylene, acetylene, propylene, and butadiene was tested for the gels $(Bu_4N)_2Fe_4S_4$ (25–100 °C), $H_2Fe_4S_4$ (25–250 °C), and $CaFe_4S_4$ (25–250 °C). No reaction products were detected in the temperature ranges listed. Turnover frequencies per Fe_4S_4 unit must have been less than 10^{-6} s^{-1}. The amount of irreversible adsorption of carbon monoxide at −78 °C was normal after these attempted reactions.

Pulses of oxygen plus hydrogen, carbon monoxide, ethylene, and 1,3-butadiene were passed over these three materials at 25–100 °C. No oxidation products were detected.

Conclusions

The experiments of this paper involved $Fe_4S_4(SR)_4{}^{2-}$ and $Fe_4S_4H_2$ in a nonpolar environment. The only possibly reactive groups near the Fe_4S_4 cores were -S–S–, -SH, and Ca^{2+}. Any CH_3O–, ≡SiOH, or ≡SiOSi≡ groups should have been deeply buried in the modifying layer. Under these conditions, the core appears to have low if any coordinative unsaturation as tested by reactivity with hydrogen and carbon monoxide and it has negligible catalytic activity for the hydrogenation and oxidation reactions which were investigated. These results do not establish that the Fe_4S_4 core is not involved in the hydrogenation activity of hydrogenase but they do not support the view that the $Fe_4S_4(SR)_4{}^{2-}$ unit *by itself* has significant hydrogenation activity in biological systems.

Of course, the experiments of this paper were designed to avoid the presence of other groups which might be near the Fe_4S_4 core in biological systems. A polar environment facilitates the oxidation of the Fe_4S_4 core and it is conceivable that it would favor heterolytic dissociation of hydrogen, where a proton goes to some basic group on the imbedding protein and a hydride ion goes to an iron atom of the core. However, one might worry as to whether the iron atom would coordinate a hydride ion when it has almost no tendency to coordinate carbon monoxide.

It should be emphasized that these conclusions apply only to $[Fe_4S_4(SR)_4]^{2-}$ units. Averill and Orme-Johnson[3] have suggested that the heterolytic dissociation of hydrogen in hydrogenase involves $[Fe_4S_4(SR)_4]^{1-}$ (although in their footnote 11, the 2− species would be indicated). However, in solution in N,N-dimethylacetamide, EPR provided evidence for reaction between carbon monoxide and the 3− species but none for the 2− species.[3] The reducing agents used to effect reduction of 2− species (like sodium acenaphthalenide) are difficultly compatible with the rather acidic silanol groups of silica gel (pK_a ~ 7–8) and it would not be easy to attach the $Fe_4S_4(SR)_4{}^{3-}$ unit to silica gel. Other supports might be possible.

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Low-Temperature NMR Studies of a Single Crystal of *trans*-Cu(DL-ala)$_2$·H_2O

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Abstract: Low-temperature NMR spectroscopy has been used to investigate a single crystal of *trans*-Cu(DL-ala)$_2$·H_2O. The lines in the NMR spectra are shifted by both the electron-nuclei dipole-dipole and Fermi contact interactions and we obtained well-resolved spectra. Analysis of these spectra yield both Cu-proton distances and proton isotropic coupling constants. The metal-proton distances obtained from this NMR study are in good agreement with distances obtained from other metal-amino acid complexes by X-ray crystallography. The isotropic coupling constants determined in this study were accounted for by a mechanism involving spin delocalization from the copper's $d_{x^2-y^2}$ orbital through the σ bonds of the amino acid. The investigation demonstrates the utility of low-temperature NMR spectroscopy for the study of the structure of transition-metal complexes.

Introduction

Low-temperature nuclear magnetic resonance investigations of solid paramagnetic molecules allow one to obtain information about both the electron–nuclei dipolar and Fermi contact (isotropic) interactions.[1,2] These interactions shift the NMR lines of nuclei in the ligands of transition-metal complexes and well-resolved spectra are observed when these shifts become large compared to the intrinsic line width of solid samples. Exchange is normally rapid in concentrated solids and the nuclei experience an averaged electron spin polarization. The spin polarization and shifts vary inversely with temperature when the susceptibility follows a Curie law and if the experiments are carried out at low enough temperature well-resolved spectra are observed. The dipolar interaction depends on the separation of the electron and nuclear spins (r_i) and on the angle between the electron–nucleus vector and the external field (θ_i). Analysis of the angular dependence of shifts from single crystals may therefore be used to obtain information about the position of ligand nuclei with respect to the central metal ion. Nuclei within about a 1-6-Å radius of the metal ion have appreciable shifts at low temperatures while more distant nuclei experience smaller dipolar fields and their shifts are small compared to the width of the signals. An NMR study therefore produces information on the local structure of ligand nuclei near the metal ion which is of particular interest for relatively large biologically important complexes in which one is interested in the structure of ligands near the metal ion.

Fermi contact interactions (isotropic hyperfine couplings) may also be obtained through an analysis of the NMR spectra of metal complexes. This term is independent of orientation and can readily be separated from the angularly dependent dipolar term. Isotropic couplings from protons in the ligands of metal complexes are generally not resolved in ESR spectra as the line width is large compared to the magnitude of these couplings. Solution NMR studies of metal–amino acid complexes are generally complicated by multiple equilibria and isotropic coupling constants cannot be obtained directly. Evaluation of isotropic coupling constants from a series of ligand nuclei allows one to obtain information on the mechanism of spin delocalization from the metal atom into the ligand. Variations in the magnitudes of these couplings with the structure of the ligand are of value in identification of the coordinated amino acid in higher molecular weight complexes. We have initiated an NMR investigation of a series of metal–amino acid and metal–peptide complexes. This paper reports the results from a study of a single crystal of *trans*-Cu(DL-ala)$_2$·H_2O.

Theoretical

Spin exchange is normally rapid in concentrated samples of metal complexes and the nuclear spins experience an averaged electron spin polarization $\langle S \rangle$. In samples in which the magnetic susceptibility follows a Curie–Weiss law the averaged electron spin polarization is given by

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